Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Palladium(II)-catalyzed stereoselective synthesis of *C*-glycosides from glycals with diaryliodonium salts

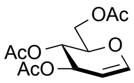
Kumar Bhaskar Pal, Jiande Lee, Mrinmoy Das and Xue-Wei Liu *

I. Experimental Procedures

I.1 General experimental procedures

All reactions were carried out in non-dried glassware. All solvents and reagents purchased from commercial sources or synthesized via literature protocol and used without further purifications. TLC analysis was performed on pre-coated Merck silica gel 60 F_{254} plates using UV light and charring solution (10 mL conc. H_2SO_4/ 90 mL EtOH). Flash column chromatography was done on SiO_2 purchased from Aldrich (technical grade, 60 Å pore size, 230-400 mesh, 40-63 µm). All NMR spectra were recorded with Bruker Avance DRX 300 MHz spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C, 282 MHz for ^{19}F), Bruker DRX 400 MHz spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, 376 MHz for ^{19}F), and Bruker Avance DRX 500 MHz spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C) at ambient temperature using $CDCl_3$, CD_3OD or $(CD_3)_2SO$ as solvents. Chemical shifts are given in ppm relative to the residual solvent peak (^1H NMR: $CDCl_3$ δ 7.26; CD_3OD δ 3.31; $(CD_3)_2SO$ δ 2.50; ^{13}C NMR: $CDCl_3$ δ 77.16; CD_3OD δ 49.00; $(CD_3)_2SO$ δ 39.52) with multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet, app = apparent), coupling constants (in Hz) and integration. High resolution mass analyses were obtained using Micromass Q-TOF mass spectrometer (ESI). Analytical data is given if the compound is novel or not fully characterized in the literature.

I.2 List of glycal donors used in the study:



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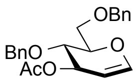

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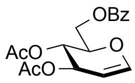

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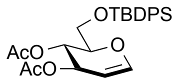

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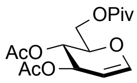

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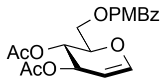

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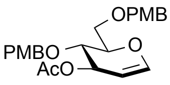

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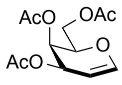

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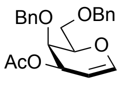

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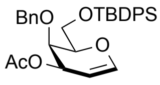

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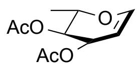

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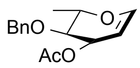

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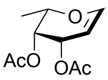

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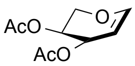

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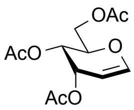

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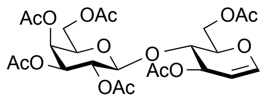

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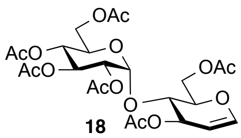

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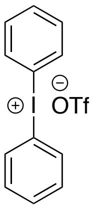
I.3 List of symmetrical aryl iodonium triflates used in the study:



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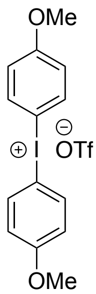

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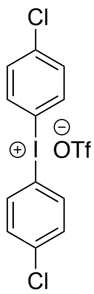

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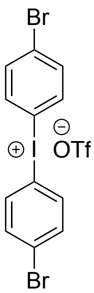

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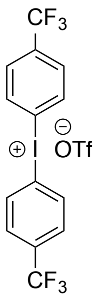

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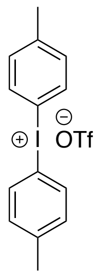

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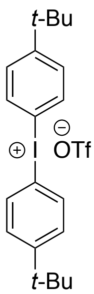

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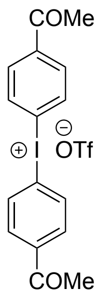

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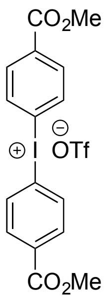

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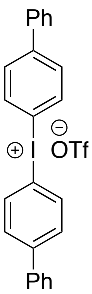

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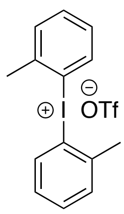

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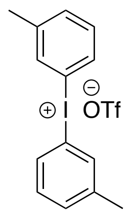

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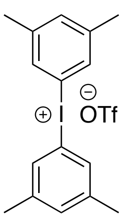

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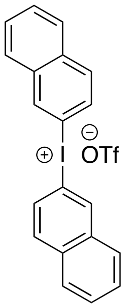

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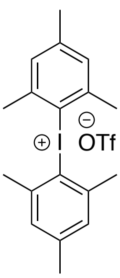

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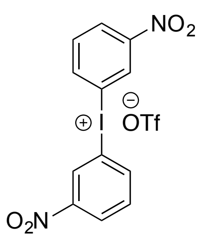

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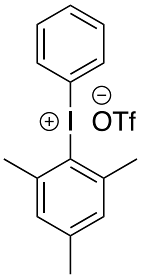

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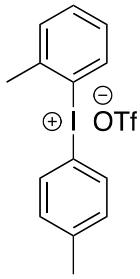

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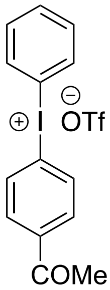

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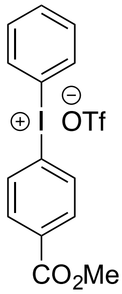

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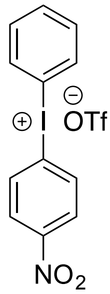

2u

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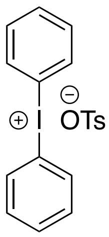

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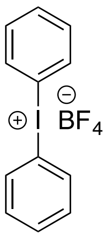
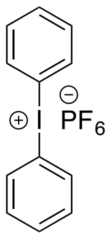


4b



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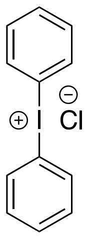

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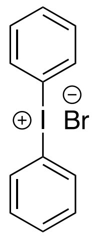

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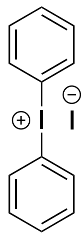


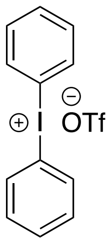
4f

I.6 General procedure for the preparation of diaryl iodonium triflates:

Iodoarene (4.00 mmol, 1 equ) was added to a solution of 3-chloroperbenzoic acid (50% active oxidant, 1.55 g, 4.4 mmol, 1.1 equ) in CH_2Cl_2 (15 mL). The mixture was stirred at 80 °C for 10 min. The solution was then cooled to 0 °C and a mixture of arylboronic acid (4.4 mmol, 1.1 equ) and $BF_3.OEt_2$ (1.2 mL, 10 mmol, 2.5 equ) in CH_2Cl_2 (15 mL) was added. The mixture was stirred for 15 min at 0 °C, and then warmed to room temperature and continued stirring for 1h. TfOH (0.37 mL) was added dropwise. The mixture was stirred for 15 min, and then concentrated under vacuum. Then Et_2O (30 mL) was added. The solid was filtered, washed thoroughly with Et_2O (30 mL×3), dried under vacuum to give diaryliodonium triflate **2**.

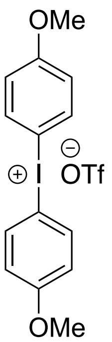
Compound **2f**, **4a**, **4c**-**4f** were purchased from the commercially available sources.

Procedure for the preparation of biphenyliodonium triflate (2a):



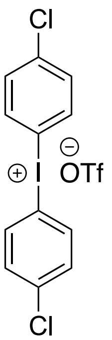
Iodobenzene (2.68 g, 4.00 mmol) was added to a solution of 3-chloroperbenzoic acid (50% active oxidant, 9.3 g, 26.4 mmol) in CH_2Cl_2 (90 mL). The mixture was stirred at 80 °C for 10 min. The solution was then cooled to 0 °C and a mixture of phenylboronic acid (3.22 g, 26.4 mmol) and $BF_3.OEt_2$ (7.2 mL, 60 mmol) in CH_2Cl_2 (90 mL) was added. The mixture was stirred for 15 min at 0 °C, and then warmed to room temperature and continued stirring for 1h. TfOH (2.22 mL) was added dropwise. The mixture was stirred for 15 min, and then concentrated under vacuum. Then Et_2O (180 mL) was added. The solid was filtered, washed thoroughly with Et_2O (150 mL×3), dried under vacuum to give diaryliodonium triflate **2a**. Obtained as a white solid in 69% yield (7.14 g, 2.32 mmol). ^1H NMR (400 MHz, $(CD_3)_2SO$) δ = 8.27 (d, *J* 7.6 Hz, 4H), 7.62 (d, *J* 7.6 Hz, 2H), 7.50 (d, *J* 7.6 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 135.3, 132.1, 131.8, 116.4, 120.9 (q, *J* 320.5 Hz), 116.4 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ = -77.6 ppm.

Procedure for the preparation of bis(4-methoxyphenyl)iodonium triflate (2b):



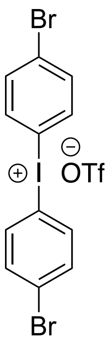
Compound **2b** was prepared according to the general procedure **I.5** from 4-iodoanisole (936 mg, 4.00 mmol) and 4-methoxyphenylboronic acid (669 mg, 4.4 mmol). Obtained as a white solid in 41% yield (803 mg, 1.64 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 8.10 (d, *J* 8.8 Hz, 4H), 7.04 (d, *J* 8.0 Hz, 4H), 3.78 (s, 6H) ppm. ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ = 162.6, 137.5, 121.2 (q, *J* 319.0 Hz), 106.1, 56.3 ppm. ^{19}F NMR (282 MHz, $(CD_3)_2SO$) δ = -77.8 ppm.

Procedure for the preparation of bis(4-chlorophenyl)iodonium triflate (2c):



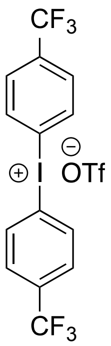
Compound **2c** was prepared according to the general procedure **I.5** from 1-chloro-4-iodobenzene (887 mg, 4.00 mmol) and 4-chlorophenylboronic acid (688 mg, 4.4 mmol). Obtained as a white solid in 30% yield (887 mg, 1.78 mmol). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ = 8.25 (d, *J* 8.4 Hz, 4H), 7.59 (d, *J* 8.7 Hz, 4H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ = 137.6, 137.1, 131.9, 120.8 (q, *J* 320.1 Hz) ppm. ^{19}F NMR (282 MHz, $(CD_3)_2SO$) δ = -77.7 ppm.

Procedure for the preparation of bis(4-bromophenyl)iodonium triflate (2d):



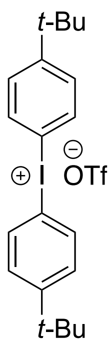
Compound **2d** was prepared according to the general procedure **I.5** from methyl 1-Bromo-4-iodobenzene (1.13 g, 4.00 mmol) and 4-bromophenylboronic acid (884 mg, 4.4 mmol). Obtained as a white solid in 43% yield (1 g, 1.71 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 8.10 (dd, *J* 2.8 Hz, *J* 11.6 Hz, 4H), 7.67 (dd, *J* 2.8 Hz, *J* 11.6 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 138.1, 136.3, 128.7, 121.8 (q, *J* 316.7 Hz), 114.2 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ = -79.8 ppm.

Procedure for the preparation of bis(4-trifluoromethylphenyl)iodonium triflate (2e):



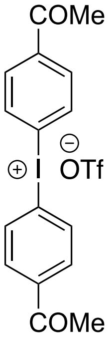
Compound **2e** was prepared according to the general procedure **I.5** from 4-iodobenzotrifluoride (588 µL, 4.00 mmol) and 4-(trifluoromethyl)phenylboronic acid (836 mg, 4.4 mmol). Obtained as a white solid in 30% yield (679 mg, 1.2 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ = 8.45 (d, *J* 8.0 Hz, 4H), 7.84 (d, *J* 8.8 Hz, 4H) ppm. ^{13}C NMR (100 MHz, CD_3OD) δ = 137.5, 135.4 (q, *J* 33.0 Hz), 129.9 (q, *J* 3.7 Hz), 124.6 (q, *J* 270.8 Hz), 121.8 (q, *J* 316.7 Hz), 119.8 ppm. ^{19}F NMR (376 MHz, CD_3OD) δ = -64.8, -79.9 ppm.

Procedure for the preparation of bis(4-tertbutylphenyl)iodonium triflate (2g):



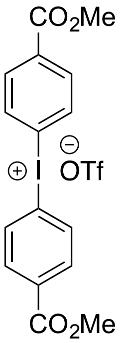
Compound **2g** was prepared according to the general procedure **I.5** from methyl 4-*tert*-butyliodobenzene (1.04 g, 4.00 mmol) and 4-*tert*-butylphenylboronic acid (783 mg, 4.4 mmol). Obtained as a white solid in 55% yield (1.19 mg, 2.2 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 8.20 (d, *J* 8.4 Hz, 4H), 7.51 (d, *J* 8.8 Hz, 4H), 1.21 (s, 18H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 155.2, 135.0, 128.8, 120.8 (q, *J* 320.4 Hz), 112.6, 34.8, 30.7 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ = -77.6 ppm.

Procedure for the preparation of bis(4-acetylphenyl)iodonium triflate (2h):



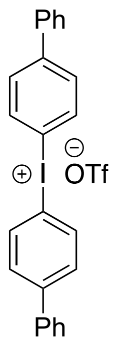
Compound **2h** was prepared according to the general procedure **I.5** from 4′-iodoacetophenone (984 mg, 4.00 mmol) and 4-acetylphenylboronic acid (722 mg, 4.4 mmol). Obtained as an off white solid in 41% yield (843 mg, 1.64 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ = 8.33 (d, *J* 8.8 Hz, 4H), 8.07 (d, *J* 8.0 Hz, 4H), 2.61 (s, 6H) ppm. ^{13}C NMR (100 MHz, CD_3OD) δ = 198.7, 142.3, 136.9, 132.5, 121.8 (q, *J* 316.7 Hz), 120.4, 26.8 ppm. ^{19}F NMR (376 MHz, CD_3OD) δ = -80.8 ppm. HRMS calcd. for $C_{16}H_{14}O_2I^+(M-TfO^-)^+$: 365.0033, found: 365.0039.

Procedure for the preparation of bis(4-carbomethoxyphenyl)iodonium triflate (2i):



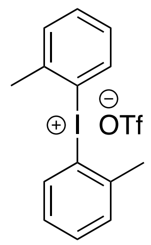
Compound **2i** was prepared according to the general procedure **I.5** from methyl 4-iodobenzoate (1.05 g, 4.00 mmol) and 4-methoxycarbonylphenylboronic acid (720 mg, 4.4 mmol). Obtained as a white solid in 33% yield (722 mg, 1.32 mmol). ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ = 8.41 (d, *J* 8.5 Hz, 4H), 8.01 (d, *J* 8.5 Hz, 4H), 3.83 (s, 6H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ = 165.2, 135.8, 132.8, 132.1, 121.5, 120.8 (q, *J* 320.5 Hz), 52.7 ppm. ^{19}F NMR (282 MHz, $(CD_3)_2SO$) δ = -77.7 ppm.

Procedure for the preparation of bis(4-biphenyl)iodonium triflate (2j):



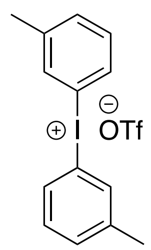
Compound **2j** was prepared according to the general procedure **I.5** from 4-iodobiphenyl (1.12 g, 4.00 mmol) and 4-biphenylboronic acid (871 mg, 4.4 mmol). Obtained as a white solid in 35% yield (815 mg, 1.4 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 8.38 (d, *J* 8.8 Hz, 4H), 7.80 (d, *J* 8.4 Hz, 4H), 7.66 (d, *J* 7.2 Hz, 4H), 7.45 (d, *J* 7.6 Hz, 4H), 7.38 (d, *J* 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 143.8, 138.1, 135.9, 129.9, 129.1, 128.7, 127.0, 120.9 (q, *J* 320.3 Hz), 116.1 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ = -77.6 ppm.

Procedure for the preparation of bis(2-tolyl)iodonium triflate (2k):



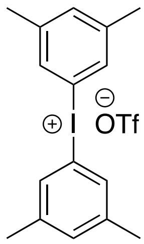
Compound **2k** was prepared according to the general procedure **I.5** from 2-iodotoluene (872 mg, 4.00 mmol) and *o*-tolylboronic acid (598 mg, 4.4 mmol). Obtained as a white solid in 61% yield (1.12 g, 2.44 mmol). ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ = 8.30 (d, *J* 7.5 Hz, 2H), 7.59-7.54 (m, 4H), 7.31-7.28 (m, 2H), 2.61 (s, 6H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 140.5, 137.1, 132.7, 131.5, 129.2, 120.7 (q, *J* 320.3 Hz), 120.4, 24.9 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ = -77.7 ppm.

Procedure for the preparation of bis(3-tolyl)iodonium triflate (2l):



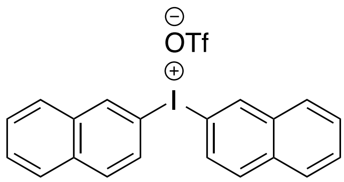
Compound **2l** was prepared according to the general procedure **I.5** from 3-iodotoluene (872 mg, 4.00 mmol) and *m*-tolylboronic acid (598 mg, 4.4 mmol). Obtained as a white solid in 65% yield (1.19 g, 2.6 mmol). ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ = 8.12 (bs, 2H), 8.05 (d, *J* 8.0 Hz, 2H), 7.46 (d, *J* 7.5 Hz, 2H), 7.40 (t, *J* 7.5 Hz, 2H), 2.33 (s, 6H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ = 141.8, 135.4, 132.7, 132.3, 131.4, 120.8 (q, *J* 320.4 Hz), 116.2, 20.7 ppm. ^{19}F NMR (282 MHz, $(CD_3)_2SO$) δ = -77.7 ppm.

Procedure for the preparation of bis(3,5-dimethylphenyl)iodonium triflate (2m):



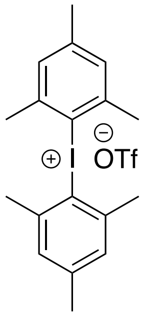
Compound **2m** was prepared according to the general procedure **I.5** from 1-iodo-3,5-dimethylbenzene (928 mg, 4.00 mmol) and 3,5-dimethylphenylboronic acid (660 mg, 4.4 mmol). Obtained as a white solid in 58% yield (1.13 g, 2.32 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 7.88 (s, 4H), 7.25 (s, 2H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 141.4, 133.4, 132.4, 120.8 (q, *J* 320.8 Hz), 115.6, 20.6 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ = -77.7 ppm.

Procedure for the preparation of bis(2-naphthyl)iodonium triflate (2n):



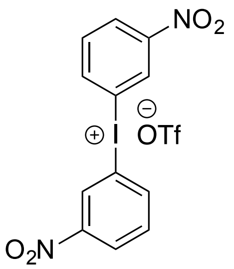
Compound **2n** was prepared according to the general procedure **I.5** from 2-iodonaphthalene (1 g, 4.00 mmol) and 2-Naphthylboronic acid (757 mg, 4.4 mmol). Obtained as a brown solid in 28% yield (584 mg, 1.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (s, 2H), 7.86 (dd, *J* 2.0 Hz, *J* 9.2 Hz, 2H), 7.80 (d, *J* 7.6 Hz, 2H), 7.72-7.69 (m, 4H), 7.49 (dquint, *J* 1.2 Hz, *J* 6.8 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.0, 134.7, 134.1, 132.2, 129.7, 129.3, 128.7, 128.1, 120.5 (q, *J* 318.0 Hz), 110.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -78.0 ppm.

Procedure for the preparation of bis(2,4,6-trimethylphenyl)iodonium triflate (2o):



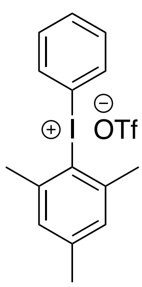
Compound **2o** was prepared according to the general procedure **I.5** from 2,4,6-trimethyliodobenzene (652 μL, 4.00 mmol) and 2,4,6-trimethylphenylboronic acid (722 mg, 4.4 mmol). Obtained as a white solid in 48% yield (987 mg, 1.92 mmol). Following the general procedure B **3c** gave as white solid, 36.0 mg, 74% yield. ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ = 7.19 (s, 4H), 2.48 (s, 12H), 2.28 (s, 6H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ = 142.8, 142.0, 130.3, 120.8 (q, *J* 320.4 Hz), 119.0, 25.4, 20.3 ppm. ^{19}F NMR (282 MHz, $(CD_3)_2SO$) δ = -77.7 ppm.

Procedure for the preparation of bis(3-nitrophenyl)iodonium triflate (2p):



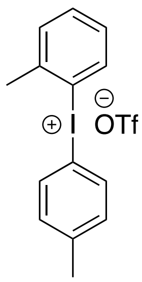
Compound **2p** was prepared according to the general procedure **I.5** from 1-iodo-3-nitrobenzene (996 mg, 4.00 mmol) and 3-nitrophenylboronic acid (735 mg, 4.4 mmol). Obtained as an off white solid in 42% yield (873 mg, 1.68 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ = 9.21 (d, *J* 2.0 Hz, 4H), 8.66 (dq, *J* 0.8 Hz, *J* 8.0 Hz, 2H), 8.53 (ddd, *J* 0.8 Hz, *J* 2.0 Hz, *J* 8.4 Hz, 2H), 7.83 (d, *J* 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CD_3OD) δ = 150.5, 142.3, 134.2, 131.5, 128.5, 120.8 (q, *J* 316.8 Hz), 115.8 ppm. ^{19}F NMR (376 MHz, CD_3OD) δ = -79.9 ppm. HRMS calcd. for $C_{12}H_8N_2O_4I^+(M\text{-}TfO^-)^+$: 370.9523, found: 370.9525.

Procedure for the preparation of (2,4,6-trimethylphenyl)(phenyl)iodonium triflate (2q):



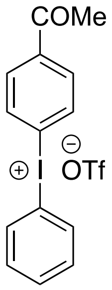
Compound **2q** was prepared according to the general procedure **I.5** from iodobenzene (448 μL, 4.00 mmol) and 2,4,6-trimethylphenylboronic acid (722 mg, 4.4 mmol). Obtained as a white solid in 57% yield (1.08 g, 2.29 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 8.01 (d, *J* 7.6 Hz, 2H), 7.61 (d, *J* 7.6 Hz, 1H), 7.50 (d, *J* 7.6 Hz, 2H), 7.19 (s, 2H), 2.63 (s, 12H), 2.25 (s, 6H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 142.8, 141.2, 134.0, 131.5, 131.3, 129.4, 122.1, 120.4 (q, *J* 320.3 Hz), 113.9, 25.9, 20.0 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ = -77.6 ppm.

Procedure for the preparation of (2-tolyl)(4-tolyl)iodonium triflate (2r):



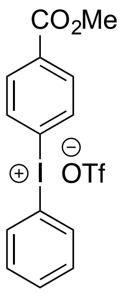
Compound **2r** was prepared according to the general procedure **I.5** from 2-iodotoluene (872 mg, 4.00 mmol) and *p*-tolylboronic acid (598 mg, 4.4 mmol). Obtained as a white solid in 55% yield (1.0 g, 2.2 mmol). ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ = 8.39 (d, *J* 8.0 Hz, 1H), 8.10 (d, *J* 8.0 Hz, 2H), 7.57-7.54 (m, 2H), 7.31-7.28 (m, 3H), 2.62 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ = 142.6, 140.6, 137.1, 135.1, 132.8, 132.5, 131.5, 129.3, 121.6, 120.8 (q, *J* 320.4 Hz), 112.3, 25.0, 20.8 ppm. ^{19}F NMR (282 MHz, $(CD_3)_2SO$) δ = -77.7 ppm.

Procedure for the preparation of (4-acetylphenyl)(phenyl)iodonium triflate (2s):



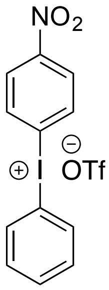
Compound **2q** was prepared according to the general procedure **I.5** from 4′-iodoacetophenone (984 mg, 4.00 mmol) and phenylboronic acid (537 mg, 4.4 mmol). Obtained as a white solid in 39% yield (736 mg, 1.56 mmol). ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ = 8.39 (d, *J* 7.5 Hz, 2H), 8.30 (d, *J* 7.0 Hz, 2H), 8.01 (d, *J* 8.5 Hz, 2H), 7.67 (t, *J* 7.0 Hz, 1H), 7.54 (d, *J* 7.5 Hz, 2H), 2.58 (s, 3H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ = 197.4, 139.1, 135.5, 135.4, 132.3, 131.9, 131.0, 121.1, 120.8 (q, *J* 320.4 Hz), 116.7, 26.9 ppm. ^{19}F NMR (282 MHz, $(CD_3)_2SO$) δ = -77.6 ppm. HRMS calcd. for $C_{14}H_{12}OI^{+}(M\text{-}TfO^{-})^{+}$: 322.9927, found: 322.9931.

Procedure for the preparation of (4-carbomethoxyphenyl)(phenyl)iodonium triflate (2t):



Compound **2t** was prepared according to the general procedure **I.5** from methyl 4-iodobenzoate (1.05 g, 4.00 mmol) and phenylboronic acid (537 mg, 4.4 mmol). Obtained as a white solid in 36% yield (704 mg, 1.44 mmol). ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ = 8.38 (d, *J* 8.5 Hz, 2H), 8.29 (d, *J* 7.5 Hz, 2H), 7.98 (d, *J* 8.5 Hz, 2H), 7.66 (t, *J* 7.5 Hz, 1H), 7.53 (d, *J* 7.5 Hz, 2H), 3.81 (s, 3H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ = 165.3, 135.7, 135.6, 132.8, 132.4, 132.1, 121.4, 120.9 (q, *J* 320.3 Hz), 116.8, 52.8 ppm. ^{19}F NMR (282 MHz, $(CD_3)_2SO$) δ = -77.7 ppm. HRMS calcd. for $C_{14}H_{12}O_2I^+(M\text{-}TfO^-)^+$: 338.9878, found: 338.9881.

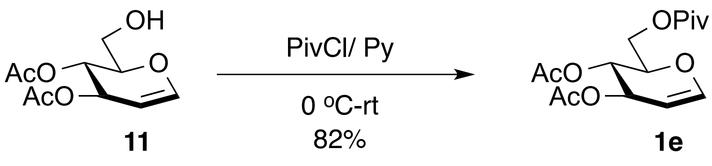
Procedure for the preparation of (4-nitrophenyl)(phenyl)iodonium triflate (2u):



Compound **2u** was prepared according to the general procedure **I.5** from 1-iodo-4-nitrobenzene (996 mg, 4.00 mmol) and phenylboronic acid (537 mg, 4.4 mmol). Obtained as a white solid in 48% yield (912 mg, 1.92 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 8.43 (dd, *J* 2.0 Hz, *J* 7.2 Hz, 4H), 8.30 (dd, *J* 2.0 Hz, *J* 7.2 Hz, 2H), 8.27 (dd, *J* 0.8 Hz, *J* 8.4 Hz, 2H), 7.73 (t, *J* 7.6 Hz, 1H), 7.57 (t, *J* 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 150.2, 136.3, 135.5, 132.8, 132.1, 126.1, 120.5 (q, *J* 316.7 Hz), 120.2, 114.8 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ = -77.7 ppm.

N.B. All the Analytical data were inagreement with previous reports.[1-3]

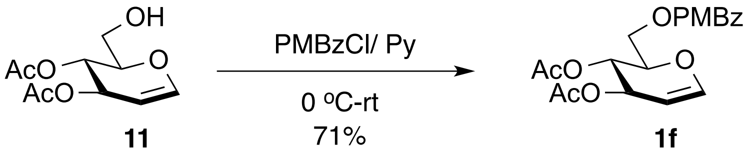
I.7 Procedure for the preparation of 3,4-Di-O-acetyl-6-O-pivaloyl-D-glucal (1e):



Scheme 2. Synthesis of 3,4-Di-*O*-acetyl-6-*O*-pivaloyl-D-glucal (**6e**).

To a 25 mL. round bottom flask 3,4-di-*O*-acetyl glucal, **11**[4] (500 mg, 2.17 mmol) was dissolved in 2 mL. of pyridine. The reaction container was placed in an ice bath (0-5 °C) and stirred for 10 minutes. After 10 minutes pivaloyl chloride (404 µL, 3.3 mmol) and a pinch of DMAP were added in the reaction mixture kept at 0 °C and the reaction mixture was stirred for 5 minutes at the mentioned temperature. Then the reaction temperature was slowly raised to the room temperature and stirred for 12 h. After which, the solvent was removed under vacuum and co-evaporated with toluene (10 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 4:1) to obtain 4,6-di-*O*-acetyl-3-*O*-pivaloyl glucal (**6d**) in 82% (559 mg, 1.78 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.44 (dd, *J* 0.8 Hz, 6.0 Hz, 1H), 5.31-5.28 (m, 1H), 5.19 (dd, *J* 5.6 Hz, 6.4 Hz, 1H), 4.82 (dd, *J* 3.6 Hz, 6.4 Hz, 1H), 4.35-4.20 (m, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.20 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.1, 170.4, 169.5, 145.8, 98.8, 74.0, 67.4, 67.3, 61.2, 38.9, 27.2, 21.0, 20.8 ppm. HRMS calcd. for $C_{15}H_{22}O_7$+H^+ $(M+H)^+$: 315.1441, found: 315.1444.

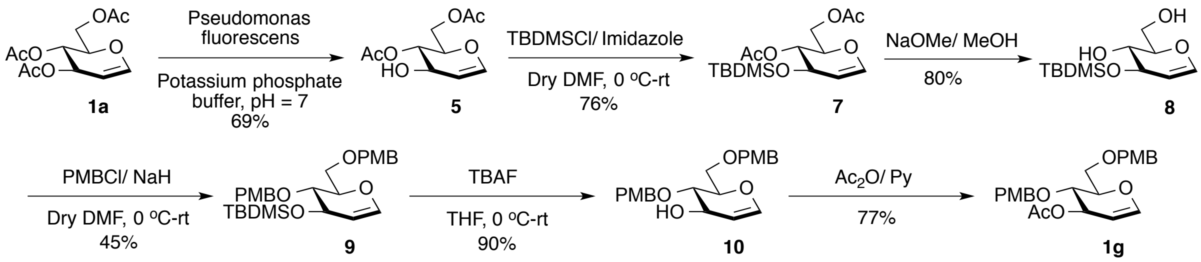
I.8 Procedure for the preparation of 3,4-Di-O-acetyl-6-O-(4-anisoyl)-D-glucal (1f):



Scheme 3. Synthesis of 3,4-Di-*O*-acetyl-6-*O*-(4-methoxy benzoyl)-D-glucal (**6e**).

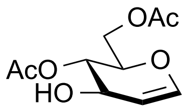
To a 25 mL. round bottom flask 3,4-di-*O*-acetyl glucal, **11**[4] (500 mg, 2.17 mmol) was dissolved in 2 mL. of pyridine. The reaction container was placed in an ice bath (0-5 °C) and stirred for 10 minutes. After 10 minutes *p*-anisoyl chloride (447 μL, 3.3 mmol) and a pinch of DMAP were added in the reaction mixture kept at 0 °C and the reaction mixture was stirred for 5 minutes at the mentioned temperature. Then the reaction temperature was slowly raised to the room temperature and stirred for 12 h. After which, the solvent was removed under vacuum and co-evaporated with toluene (10 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 2:1) to obtain 4,6-di-*O*-acetyl-3-*O*-benzoyl glucal (**6c**) in 71% (561 mg, 1.54 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02-7.99 (m, 2H), 6.94-6.91 (m, 2H), 6.49 (dd, *J* 0.8 Hz, 6.0 Hz, 1H), 5.37-5.31 (m, 2H), 4.86 (dd, *J* 3.2 Hz, 6.4 Hz, 1H), 4.54 (dd, *J* 4.0 Hz, 8.4 Hz, 1H), 4.49 (dd, *J* 12.0 Hz, 5.6 Hz, 1H), 4.42-4.38 (m, 1H), 3.85 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.5, 169.7, 166.0, 163.8, 146.0, 132.0, 122.2, 113.9, 99.0, 74.2, 67.7, 67.4, 61.8, 55.6, 21.1, 20.9 ppm. HRMS calcd. for $C_{22}H_{22}O_6$+H^+ $(M+H)^+$: 383.1495, found: 383.1499.

I.9 Procedure for the preparation of 3-O-acetyl-4,6-di-O-(4-methoxybenzyl)-D-glucal (1g):



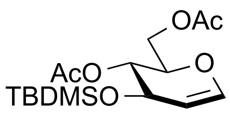
Scheme 1. Synthesis of 3-*O*-acetyl-4,6-di-*O*-(4-methoxybenzyl)-D-glucal (**1g**).

Procedure for the preparation of 4,6-Di-*O*-4-acetyl D-glucal (5):



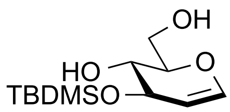
To a 500 mL. round bottom flask 3,4,6-tri-*O*-acetyl-glucal, **1a** (12 g, 44.1 mmol) and Pseudomonas Fluorescens (12 g) were taken. Into the reaction flask 120 mL. 0.1 (M) potassium phosphate buffer (pH = 7) was added and the reaction mixture was stirred for 4 h. After 4 h (when the TLC showed complete consumption of the starting material), 150 mL. EtOAc and 150 mL of brine solution were added and stirred for 30 minutes. The organic layer was collected, further washed with 150 mL. of brine solution and dried over anhydrous Na_2SO_4. After which, the solvent was removed under vacuum and the crude material was purified by flash column chromatography (hexane:EtOAc = 1:1) to obtain 4,6-di-*O*-acetyl glucal (**5**) in 69% (7 g, 30.4 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.40 (dd, *J* 1.2 Hz, *J* 6.0 Hz, 1H), 4.98 (dd, *J* 6.0 Hz, 8.8 Hz, 1H), 4.86 (dd, *J* 2.8 Hz, *J* 6.0 Hz, 1H), 4.40 (dd, *J* 5.6 Hz, *J* 8.4 Hz, 1H), 4.31 (t, *J* 6.0 Hz, 1H), 4.25 (dd, *J* 2.8 Hz, *J* 12.4 Hz, 1H), 4.15-4.11 (m, 1H), 2.48 (d, *J* 5.6 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 170.8, 144.2, 103.1, 74.2, 71.9, 67.3, 62.0, 21.1, 20.9 ppm. HRMS calcd. for $C_{10}H_{14}O_6$+Na^+ $(M+Na)^+$: 253.0688, found: 253.0691.

Procedure for the preparation of 4,6-Di-*O*-acetyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal (7):



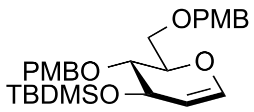
4,6-di-*O*-acetyl glucal, **5** (3 g, 13.0 mmol) and imidazole (1.77 g, 26 mmol) were dissolved in 25 mL. of dry DMF and the reaction flask was placed in an ice-bath. Then into the reaction mixture *tert*-butyldimethylsilyl chloride (2.94 g, 19.5 mmol) was added and the reaction was stirred in the ice-bath for 10 minutes then the reaction temperature was raised to room temperature and the further stirred for 16 h. After that, the solvent was removed under vacuum and the crude material was dissolved in 50 mL EtOAc and it was successively washed with water (100 mL) and sat. brine solution (100 mL). Then the organic layer was collected, dried over Na_2SO_4 and purified by flash column chromatography (hexane:EtOAc = 20:1) to obtain 4,6-di-*O*-acetyl-3-*O*-tert-butyldimethylsilyl glucal (**7**) in 76% (3.4 g, 9.9 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.32 (dd, *J* 0.8 Hz, *J* 6.4 Hz, 1H), 5.03 (t, *J* 6.0 Hz, 1H), 4.74 (dd, *J* 3.6 Hz, *J* 6.4 Hz, 1H), 4.40 (dd, *J* 6.4 Hz, *J* 12.0 Hz, 1H), 4.21-4.13 (m, 3H), 2.063 (s, 3H), 2.059 (s, 3H), 0.86 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 169.7, 143.2, 103.0, 74.1, 70.5, 65.1, 62.1, 25.7, 21.1, 20.9, 18.0, -4.5, -4.8 ppm. HRMS calcd. for $C_{16}H_{28}O_6Si+H^+$ $(M+H)^+$: 345.1733, found: 345.1731.

Procedure for the preparation of 3-*O*-(dimethyltertiarybutylsilyl)-D-glucal (8):



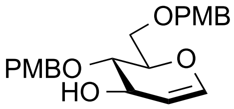
3-*O*-tert-butyldimethylsilyl glucal, **7** (3.4 g, 9.9 mmol) was dissolved in 30 mL MeOH followed by the addition of freshly prepared NaOMe in MeOH (20 mL). The reaction mixture was allowed to stir at rt for 4 h till TLC (CH_2Cl_2:MeOH; 3:1) showed complete conversion of the starting material. Then the solvent was evaporated under vaccum and the crude material was purified by flash column chromatography (hexane:EtOAc = 3:1) to obtain 3-*O*-tert-butyldimethylsilyl glucal (**8**) in 80% (2.06 g, 7.9 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.30 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 4.66 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 4.25-4.22 (m, 1H), 3.93-3.90 (m, 3H), 3.81-3.76 (m, 1H), 2.42 (d, *J* 4.8 Hz, 1H), 4.25 (t, *J* 5.2 Hz, 1H), 0.91 (s, 9H), -0.12 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.7, 103.6, 77.9, 70.8, 69.9, 62.3, 25.9, 18.2, -4.2, -4.4 ppm. HRMS calcd. for $C_{12}H_{24}O_4Si+Na^+$ $(M+Na)^+$: 283.1342, found: 283.1346.

Procedure for the preparation of 4,6-di-*O*-4-methoxybenzyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal (9):



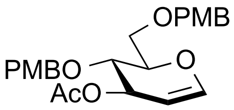
A solution of compound **8** (2.06 g, 7.9 mmol) in dry DMF (25 mL) was cooled to 0 °C. Then into the solution sodium hydride (60% dispersion in mineral oil) (760 mg, 31.6 mmol) was added in pinch by pinch. *p*-Methoxybenzyl chloride (3.2 mL, 23.7 mmol) was added dropwise over 10 min and the solution stirred at room temperature for 1 h. The reaction was poured over ice cooled water (100 mL) and extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine (200 mL). The resulting organic phase was dried (anhydrous Na_2SO_4) and filtered, and the filtrate concentrated under reduced pressure to obtain the crude mixture. The product was purified by silica gel flash column chromatography by eluting with 15:1, hexane/EtOAc. The product fractions were combined, concentrated, dried in vacuum and compound **9** (1.78 g, 3.56 mmol, 45%) was obtained as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 (d, *J* 8.8 Hz, 2H), 7.15 (d, *J* 8.8 Hz, 2H), 6.85 (t, *J* 8.4 Hz, 4H), 6.32 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 4.72 (d, *J* 10.8 Hz, 1H), 4.63 (dd, *J* 2.8 Hz, *J* 10.4 Hz, 1H), 4.53 (d, *J* 10.8 Hz, 1H), 4.51 (d, *J* 11.6 Hz, 1H), 4.48 (d, *J* 11.6 Hz, 1H), 4.32 (dq, *J* 1.2 Hz, 6.0 Hz, 1H), 4.04-4.00 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.73 (dd, *J* 5.6 Hz, 10.8 Hz, 1H), 3.65 (dd, *J* 2.4 Hz, 10.8 Hz, 1H), 3.61 (dd, *J* 2.4 Hz, 8.4 Hz, 1H), 0.90 (s, 9H), 0.09 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.5, 143.5, 130.6, 129.6, 114.0, 103.7, 76.9, 76.8, 73.7, 73.3, 69.3, 68.6, 55.44, 55.42, 26.0, 18.2, -4.2, -4.4 ppm. HRMS calcd. for $C_{28}H_{40}O_6Si+H^+$ $(M+H)^+$: 501.2672, found: 501.2670.

Procedure for the preparation of 4,6-di-*O*-4-methoxybenzyl-D-glucal (10):



A solution of compound **9** (1.78 g, 3.56 mmol) in THF (25 mL) was cooled to 0 °C. Then into the solution tetrabutylammonium fluoride solution (1.0 M in THF, 4.3 mL, 4.3 mmol) was added dropwise over 5 min and the solution stirred at 0 °C for 5 minutes and raised to room temperature. After stirring the reaction mixture for 12h at rt, the reaction mixture was concentrated under reduced pressure to obtain the crude mixture. The product was purified by silica gel flash column chromatography by eluting with 3:1, hexane/EtOAc to obtained compound **10** (1.24 g, 3.2 mmol, 90%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-6.84 (m, 8H), 4.71 (dd, *J* 2.8 Hz, 6.0 Hz, 1H), 4.68 (d, *J* 11.2 Hz, 1H), 4.60 (d, *J* 11.2 Hz, 2H), 4.58 (d, *J* 11.6 Hz, 1H), 4.50 (d, *J* 11.6 Hz, 1H), 4.29 (d, *J* 5.2 Hz, 1H), 3.97-3.93 (m, 1H), 3.81-3.76 (m, 8H), 3.63 (dd, *J* 6.4 Hz, *J* 9.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.54, 159.47, 144.6, 130.5, 130.0, 129.8, 129.7, 114.1, 114.0, 102.8, 77.0, 76.9, 73.5, 73.4, 69.1, 68.6, 55.4 ppm. HRMS calcd. for $C_{22}H_{26}O_6Si+H^+$ $(M+H)^+$: 387.1808, found: 387.1807.

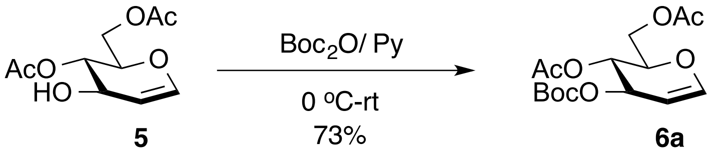
Procedure for the preparation of 3-*O*-acetyl-4,6-di-*O*-4-methoxybenzyl-D-glucal (11):



To a 25 mL. round bottom flask 4,6-di-*O*-(4-methoxybenzyl)-glucal, **10** (1.24 g, 3.2 mmol) was dissolved in 10 mL of pyridine. The reaction container was placed in an ice bath (0-5 °C) and stirred for 10 minutes. After 10 minutes 10 mL acetic anhydride and a pinch of DMAP were added in the reaction mixture kept at 0 °C and the reaction mixture was stirred for 5 minutes at 0 °C temperature. Then the reaction temperature was slowly raised to the room temperature and stirred for 12 h. After which, the solvent was removed under vacuum and co-evaporated with toluene (25 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 5:1) to obtain 3-*O*-acetyl-4,6-

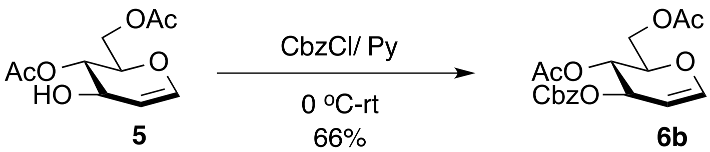
di-*O*-4-methoxybenzyl-D-glucal (**11**) in 77% (1.06 g, 2.47 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 (d, *J* 8.8 Hz, 2H), 7.16 (d, *J* 8.8 Hz, 2H), 6.88 (dd, *J* 2.0 Hz, 6.8 Hz, 2H), 6.84 (dd, *J* 2.0 Hz, 6.8 Hz, 2H), 6.43 (dd, *J* 1.2 Hz, 6.4 Hz, 1H), 5.39 (dq, *J* 1.2 Hz, *J* 6.0 Hz, 1H), 4.74 (dd, *J* 2.8 Hz, *J* 6.0 Hz, 1H), 4.60 (d, *J* 11.2 Hz, 1H), 4.55 (d, *J* 10.8 Hz, 1H), 4.53 (d, *J* 10.4 Hz, 1H), 4.48 (d, *J* 12.0 Hz, 1H), 4.07-4.03 (m, 1H), 3.88 (dd, *J* 6.4 Hz, *J* 8.8 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.77 (dd, *J* 4.4 Hz, 10.8 Hz, 1H), 3.70 (dd, *J* 3.2 Hz, 10.8 Hz, 1H), 2.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.7, 159.51, 159.48, 146.0, 130.2, 130.1, 129.7, 129.6, 113.98, 113.97, 99.3, 77.3, 73.4, 73.3, 73.0, 71.1, 67.9, 55.4, 21.4 ppm. HRMS calcd. for $C_{24}H_{28}O_7$+Na^+ $(M+Na)^+$: 451.1735, found: 451.1733.

I.10 Procedure for the preparation of 4,6-Di-O-acetyl-3-O-tert-butoxycarbonyl-D-glucal (6a):



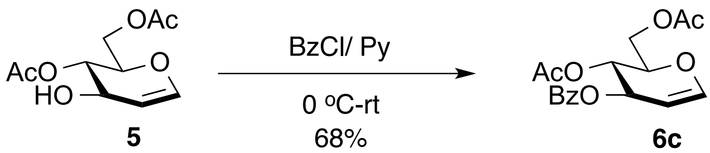
To a 25 mL. round bottom flask 4,6-di-*O*-acetyl glucal, **5** (500 mg, 2.17 mmol) was dissolved in 2 mL. of pyridine. The reaction container was placed in an ice bath (0-5 °C) and stirred for 10 minutes. After 10 minutes di-*tert*-butyl decarbonate (760 μL) and a pinch of DMAP were added in the reaction mixture kept at 0 °C and the reaction mixture was stirred for 5 minutes at the mentioned temperature. Then the reaction temperature was slowly raised to the room temperature and stirred for 12 h. After which, the solvent was removed under vacuum and co-evaporated with toluene (10 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 3:1) to obtain 4,6-di-*O*-acetyl-3-*O*-tert-butyloxycarbonyl glucal (**6a**) in 73% (524 mg, 1.59 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.46 (dd, *J* 1.2 Hz, *J* 6.4 Hz, 1H), 5.25 (dd, *J* 5.2 Hz, 8.0 Hz, 1H), 5.20-5.18 (m, 1H), 4.97 (dd, *J* 3.2 Hz, *J* 6.4 Hz, 1H), 4.88 (dd, 3.2 Hz, *J* 6.0 Hz, 1H), 4.41 (dd, *J* 5.6 Hz, *J* 12.0 Hz, 1H), 4.26-4.22 (m, 1H), 4.19 (dd, *J* 2.8 Hz, *J* 12.0 Hz, 1H, 1H), 2.084 (s, 3H), 2.079 (s, 3H) , 1.47 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.7, 169.6, 153.1, 145.9, 99.1, 82.9, 74.2, 70.3, 67.7, 61.7, 27.9, 20.9, 20.8 ppm. HRMS calcd. for $C_{15}H_{22}O_8$+H^+ $(M+H)^+$: 331.1380, found: 331.1393.

I.11 Procedure for the preparation of 4,6-Di-O-acetyl-3-O-benzyloxycarbonyl-D-glucal (6b):



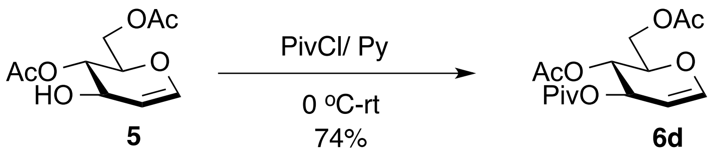
To a 25 mL. round bottom flask 4,6-di-*O*-acetyl glucal, **5** (500 mg, 2.17 mmol) was dissolved in 2 mL. of pyridine. The reaction container was placed in an ice bath (0-5 °C) and stirred for 10 minutes. After 10 minutes benzyl chloroformate (470 μL, 3.3 mmol) and a pinch of DMAP were added in the reaction mixture kept at 0 °C and the reaction mixture was stirred for 5 minutes at the mentioned temperature. Then the reaction temperature was slowly raised to the room temperature and stirred for 12 h. After which, the solvent was removed under vacuum and co-evaporated with toluene (10 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 4:1) to obtain 4,6-di-*O*-acetyl-3-*O*-benzyloxycarbonyl glucal (**6b**) in 66% (522 mg, 1.43 mmol) yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37-7.33 (m, 5H), 6.47 (dd, *J* 1.0 Hz, *J* 6.0 Hz, 1H), 5.26 (dd, *J* 5.5 Hz, 7.5 Hz, 1H), 5.23-5.21 (m, 1H), 5.10 (s, 2H), 4.92 (dd, *J* 3.0 Hz, *J* 6.0 Hz, 1H), 4.40 (dd, 5.5 Hz, *J* 7.6 Hz, 1H), 4.23-4.27 (m, 1H), 4.17 (dd, *J* 1.5 Hz, *J* 7.5 Hz, 1H, 1H), 2.07 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.7, 169.6, 154.6, 146.2, 135.1, 128.7, 128,4, 98.5, 74.1, 71.2, 70.0, 67.2, 61.5, 27.87, 20.86 ppm. HRMS calcd. for $C_{18}H_{20}O_8$+H$^+$ (M+H)$^+$: 365.1240, found: 365.1236.

I.12 Procedure for the preparation of 4,6-Di-O-acetyl-3-O-benzoyl-D-glucal (6c):



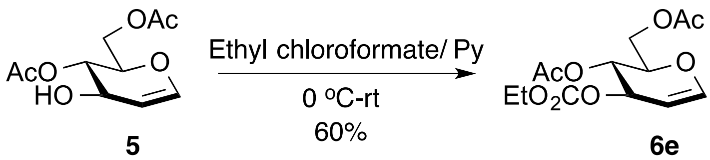
To a 25 mL. round bottom flask 4,6-di-*O*-acetyl glucal, **5** (500 mg, 2.17 mmol) was dissolved in 2 mL. of pyridine. The reaction container was placed in an ice bath (0-5 °C) and stirred for 10 minutes. After 10 minutes benzoyl chloride (384 μL, 3.3 mmol) and a pinch of DMAP were added in the reaction mixture kept at 0 °C and the reaction mixture was stirred for 5 minutes at the mentioned temperature. Then the reaction temperature was slowly raised to the room temperature and stirred for 12 h. After which, the solvent was removed under vacuum and co-evaporated with toluene (10 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 2:1) to obtain 4,6-di-*O*-acetyl-3-*O*-benzoyl glucal (**6c**) in 68% (494 mg, 1.48 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99-7.39 (m, 5H), 6.49 (dd, *J* 1.2 Hz, *J* 6.0 Hz, 1H), 5.54-5.52 (m, 1H), 5.41 (dd, *J* 5.6 Hz, 7.6 Hz, 1H), 4.97 (dd, *J* 3.2 Hz, *J* 6.4 Hz, 1H), 4.48 (dd, *J* 6.0 Hz, *J* 12.4 Hz, 1H), 4.34-4.30 (m, 1H), 4.23 (dd, *J* 3.2 Hz, *J* 12.0 Hz, 1H, 3H), 2.06 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.6, 169.5, 165.9, 145.8, 133.3, 129.7, 128.5, 99.1, 74.0, 68.2, 67.1, 61.5, 20.8, 20.7 ppm. HRMS calcd. for $C_{17}H_{18}O_7$+H$^+$ (M+H)$^+$: 335.1131, found: 335.1135.

I.13 Procedure for the preparation of 4,6-Di-O-acetyl-3-O-pivaloyl-D-glucal (6d):



To a 25 mL. round bottom flask 4,6-di-*O*-acetyl glucal, **5** (500 mg, 2.17 mmol) was dissolved in 2 mL. of pyridine. The reaction container was placed in an ice bath (0-5 °C) and stirred for 10 minutes. After 10 minutes pivaloyl chloride (404 μL, 3.3 mmol) and a pinch of DMAP were added in the reaction mixture kept at 0 °C and the reaction mixture was stirred for 5 minutes at the mentioned temperature. Then the reaction temperature was slowly raised to the room temperature and stirred for 12 h. After which, the solvent was removed under vacuum and co-evaporated with toluene (10 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 4:1) to obtain 4,6-di-*O*-acetyl-3-*O*-pivaloyl glucal (**6d**) in 74% (506 mg, 1.61 mmol) yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.39 (dd, *J* 1.2 Hz, *J* 6.4 Hz, 1H), 5.23-5.21 (m, 1H), 5.18 (dd, *J* 5.6 Hz, 7.2 Hz, 1H), 4.79 (dd, *J* 2.8 Hz, *J* 6.0 Hz, 1H), 4.37 (dd, 6.0 Hz, *J* 12.0 Hz, 1H), 4.24-4.20 (m, 1H), 4.10 (dd, *J* 2.8 Hz, *J* 12.0 Hz, 1H, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.11 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 177.7, 170.5, 169.3, 145.5, 99.1, 73.9, 67.2, 67.1, 61.5, 38.7, 27.0, 20.7 ppm. HRMS calcd. for $C_{15}H_{22}O_7$+H^+ $(M+H)^+$: 315.1444, found: 315.1446.

I.14 Procedure for the preparation of 4,6-Di-O-acetyl-3-O-ethoxycarbonyl-D-glucal (6e):



To a 25 mL. round bottom flask 4,6-di-*O*-acetyl glucal, **5** (500 mg, 2.17 mmol) was dissolved in 2 mL. of pyridine. The reaction container was placed in an ice bath (0-5 °C) and stirred for 10 minutes. After 10 minutes ethyl chloroformate (315 μL, 3.3 mmol) and a pinch of DMAP were added in the reaction mixture kept at 0 °C and the reaction mixture was stirred for 5 minutes at the mentioned temperature. Then the reaction temperature was slowly raised to the room temperature and stirred for 12 h. After which, the solvent was removed under vacuum and co-evaporated with toluene (10 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 4:1) to obtain 4,6-di-*O*-acetyl-3-*O*-ethoxycarbonyl glucal (**6e**) in 60% (394 mg, 1.3 mmol) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ =

6.85 (dd, *J* 0.8 Hz, *J* 6.0 Hz, 1H), 5.19 (dd, *J* 5.6 Hz, 7.6 Hz, 1H), 5.15-5.13 (m, 1H), 4.87 (dd, *J* 3.2 Hz, *J* 6.0 Hz, 1H), 4.37 (dd, *J* 6.0 Hz, *J* 12.4 Hz, 1H), 4.23-4.19 (m, 1H), 4.17-4.11 (m, 3H), 2.041 (s, 3H), 2.039 (s, 3H), 1.25 (t, 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.5, 169.6, 166.2, 145.9, 133.3, 129.8, 128.6, 99.0, 74.1, 67.7, 67.4, 62.0, 21.1, 20.9 ppm. HRMS calcd. for $C_{13}H_{18}O_8+H^+$ $(M+H)^+$: 303.1080, found: 303.1080.

II. References

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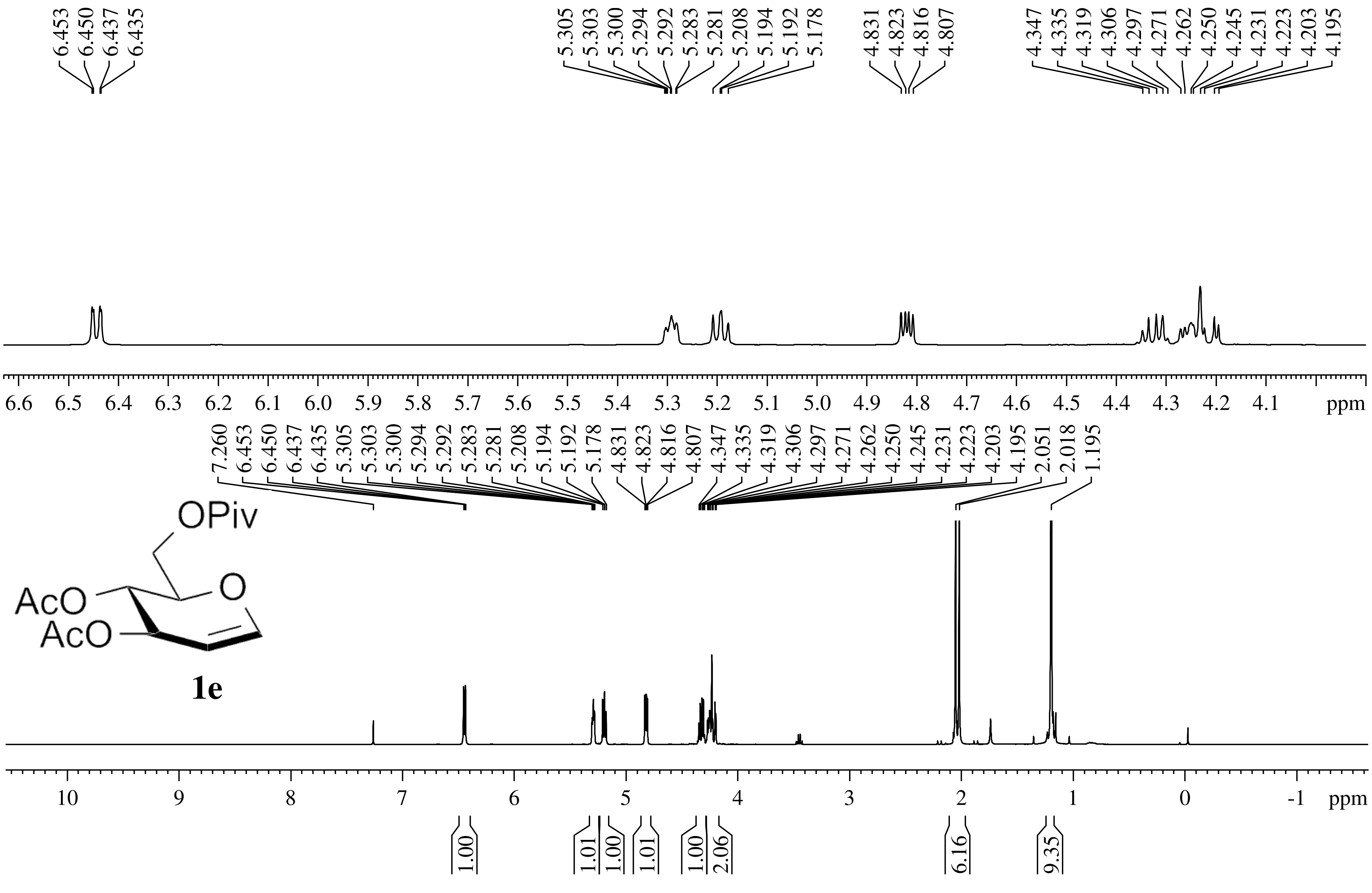
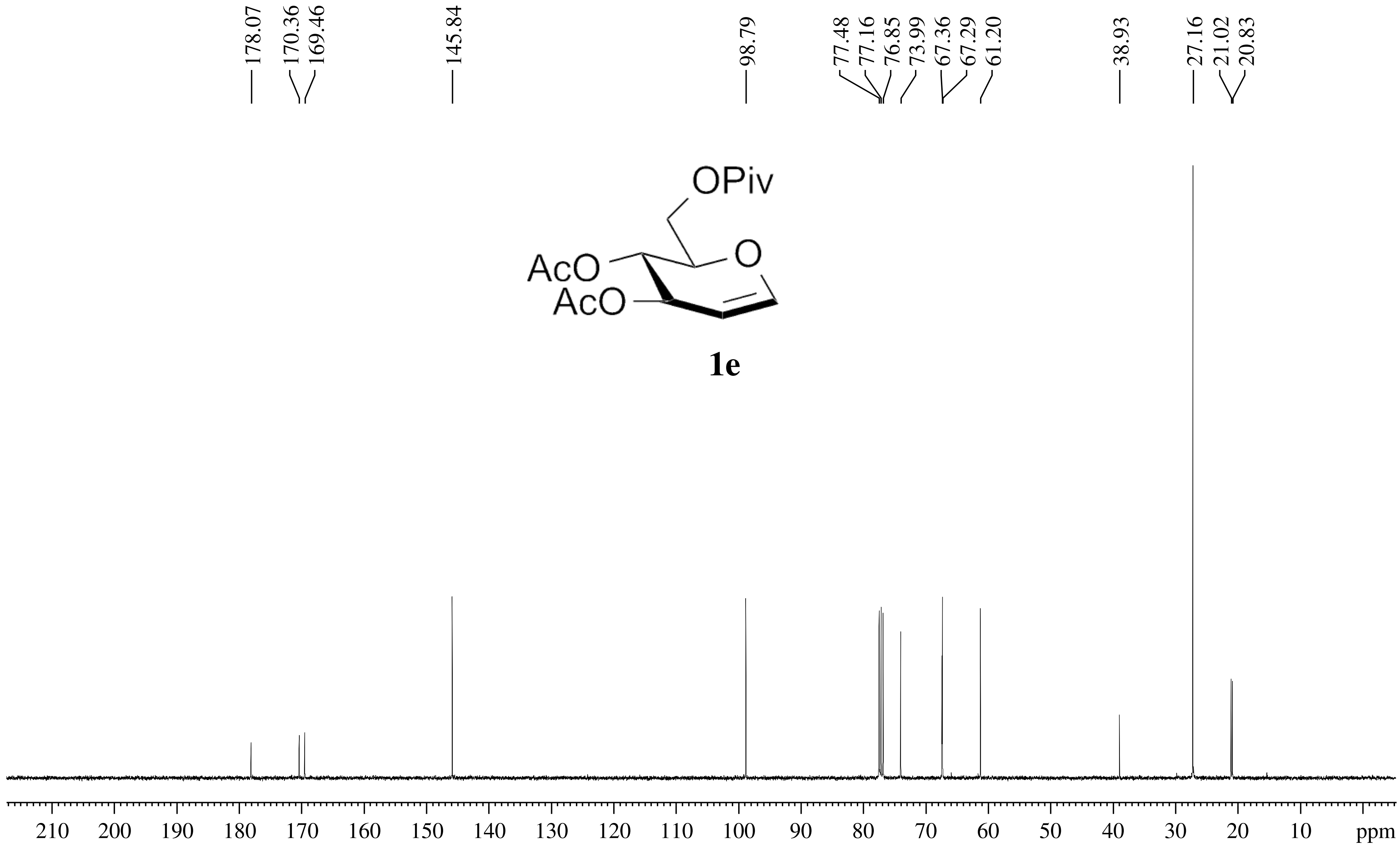
III. Copy of NMR Spectra

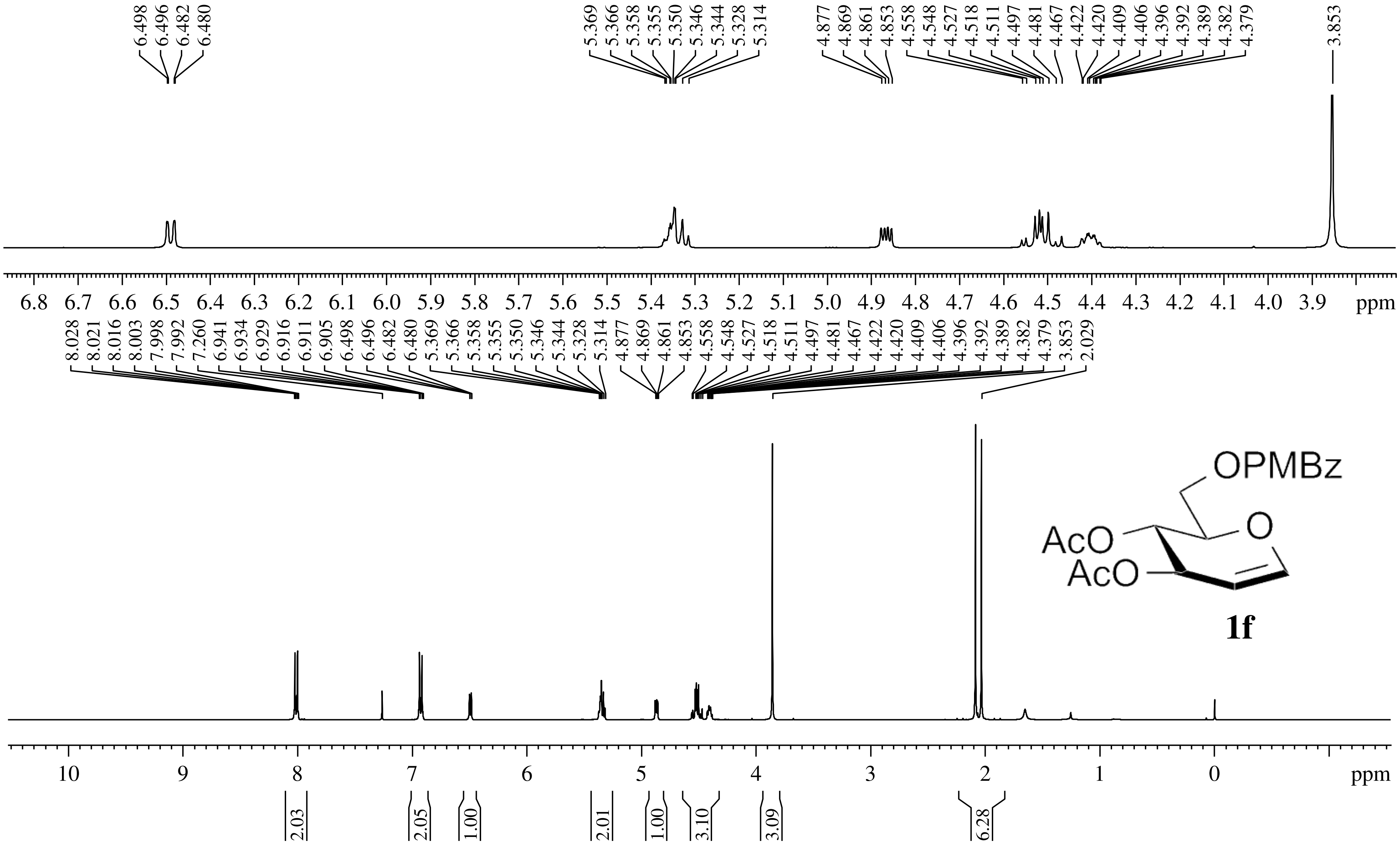
^{1}H NMR, $CDCl_3$, 400 MHz



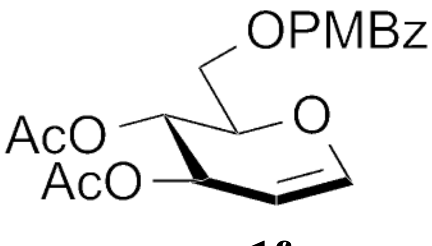
^{13}C NMR, $CDCl_3$, 100 MHz



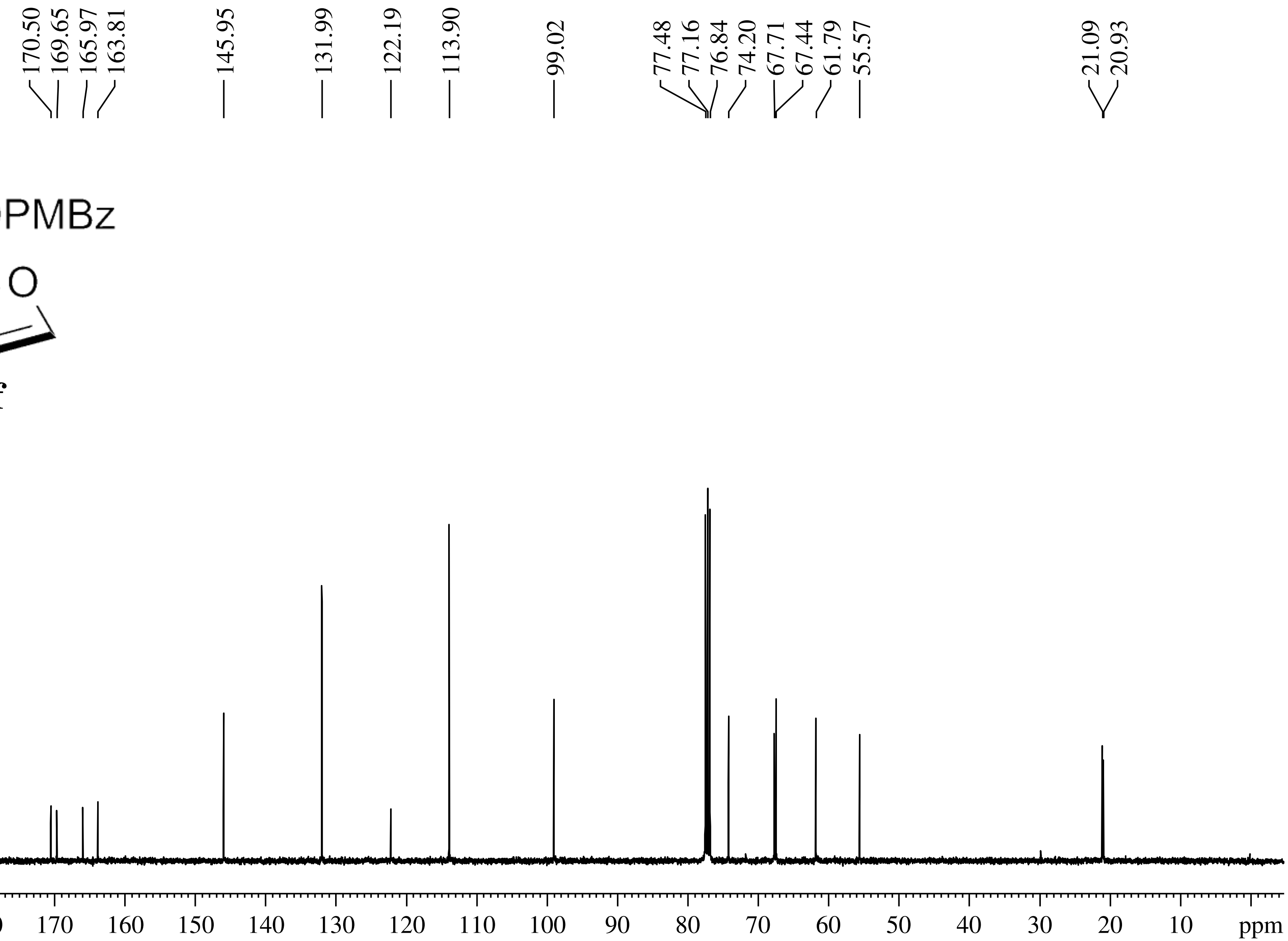
^1H NMR, $CDCl_3$, 400 MHz



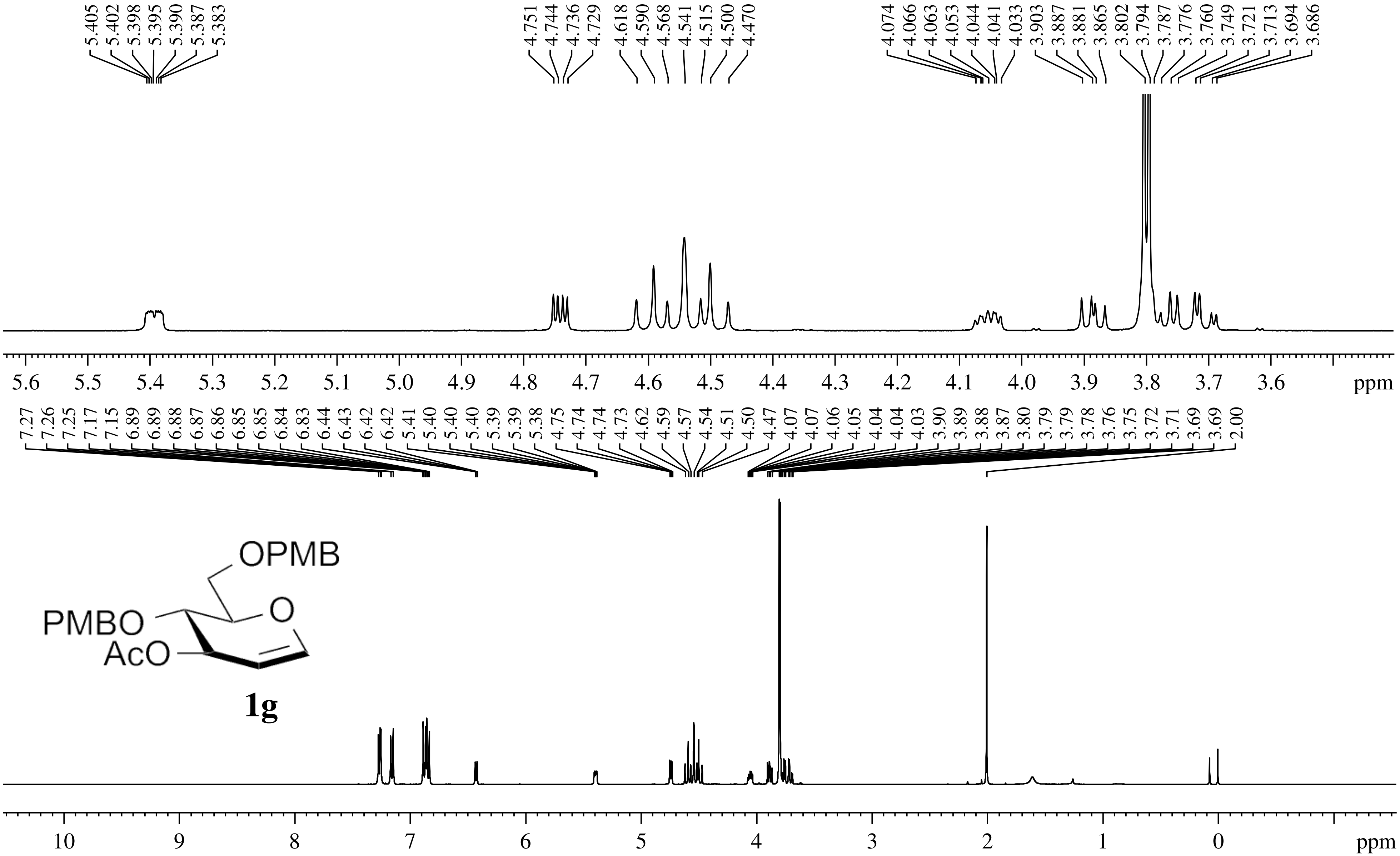
^{13}C NMR, $CDCl_3$, 100 MHz



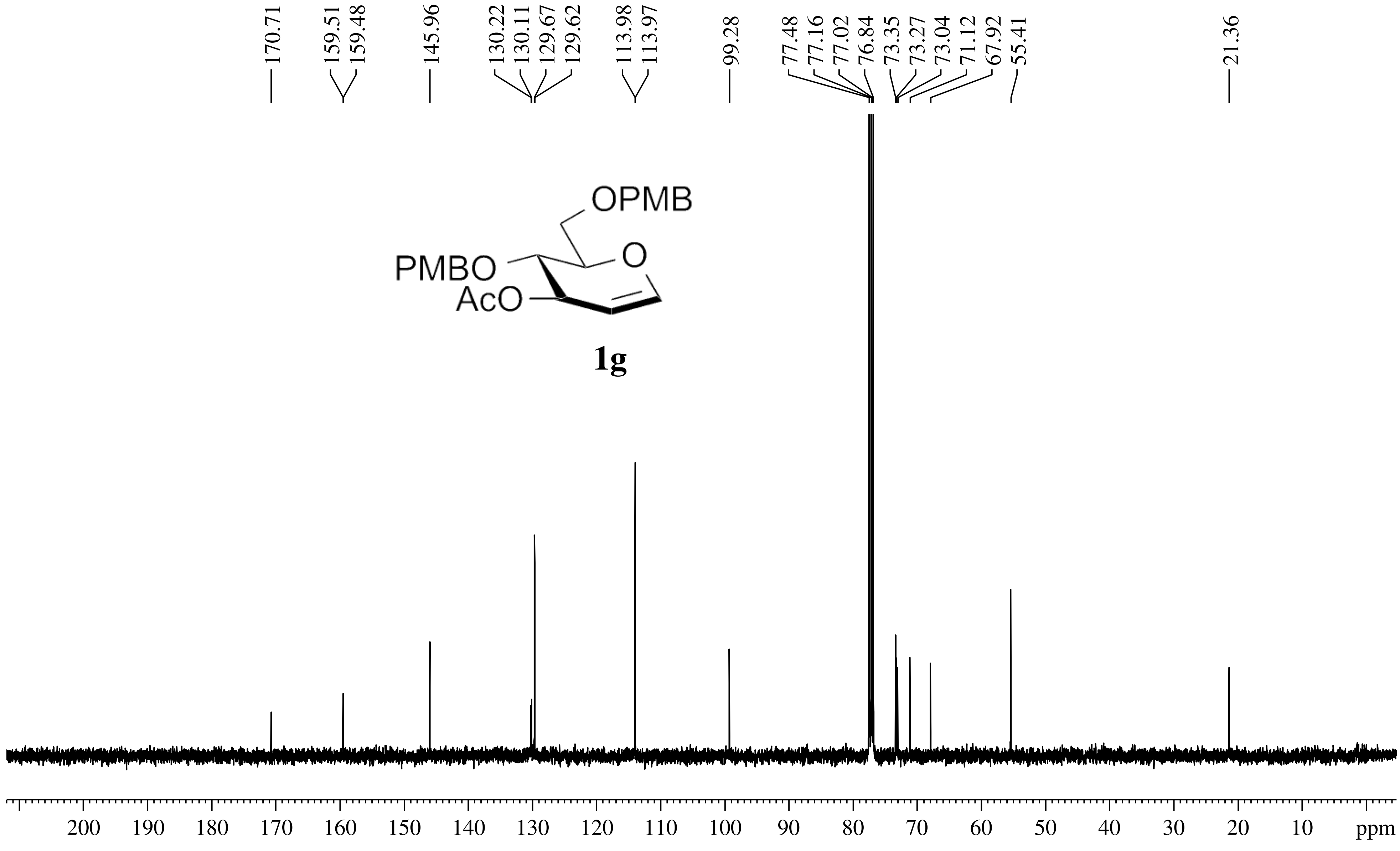
1f



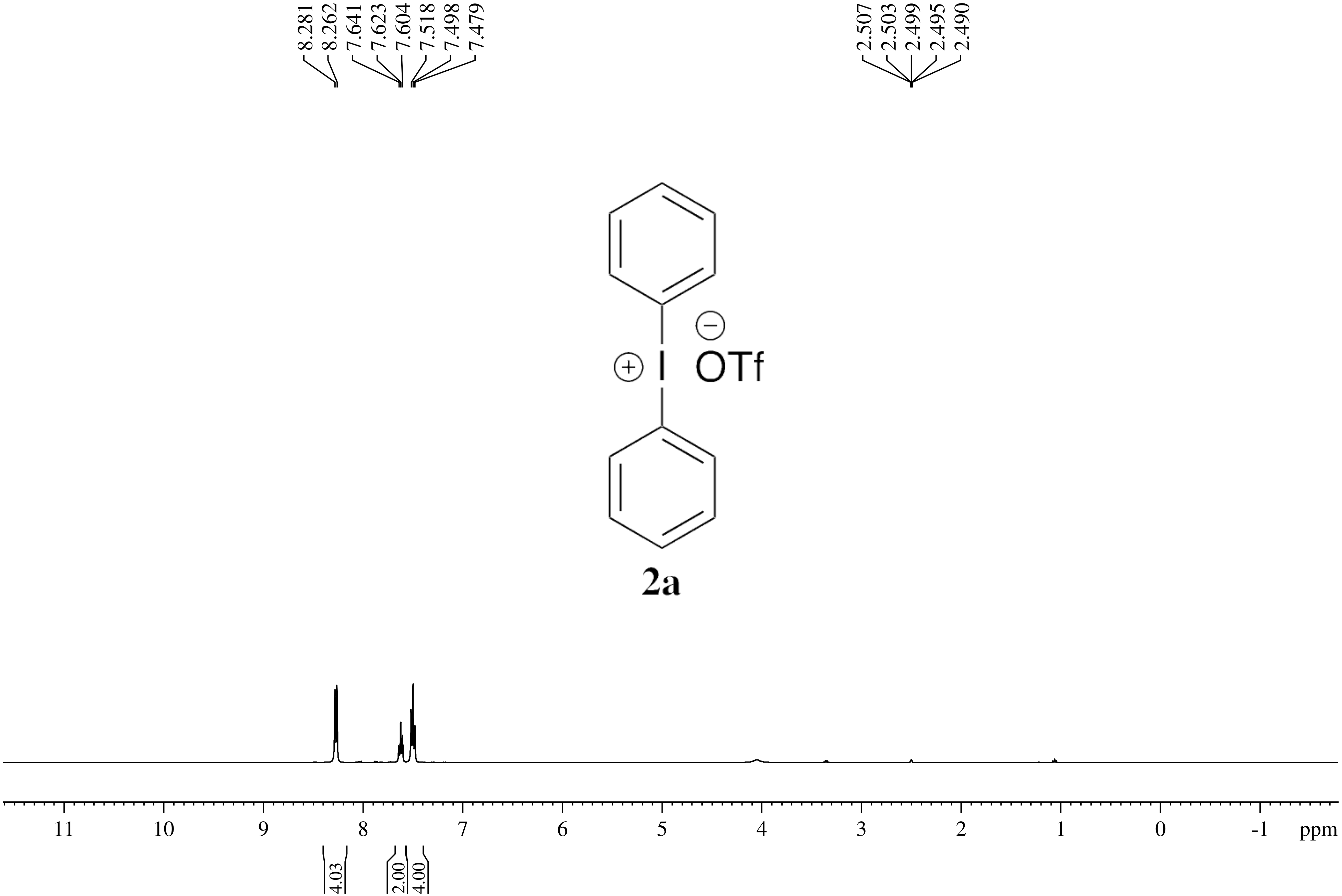
^{1}H NMR, $CDCl_3$, 400 MHz



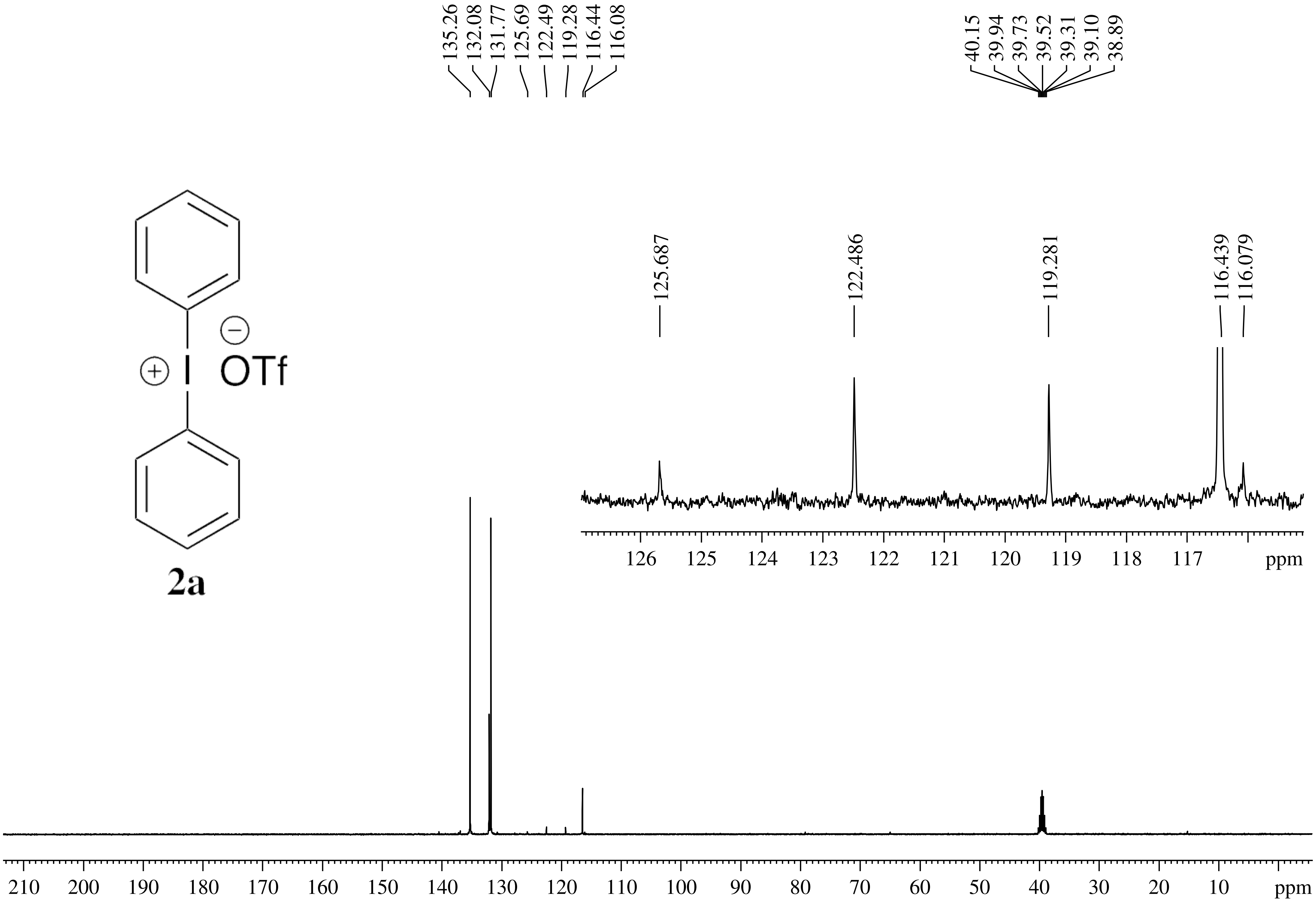
^{13}C NMR, $CDCl_3$, 100 MHz



^{1}H NMR, $(CD_3)_2SO$, 400 MHz

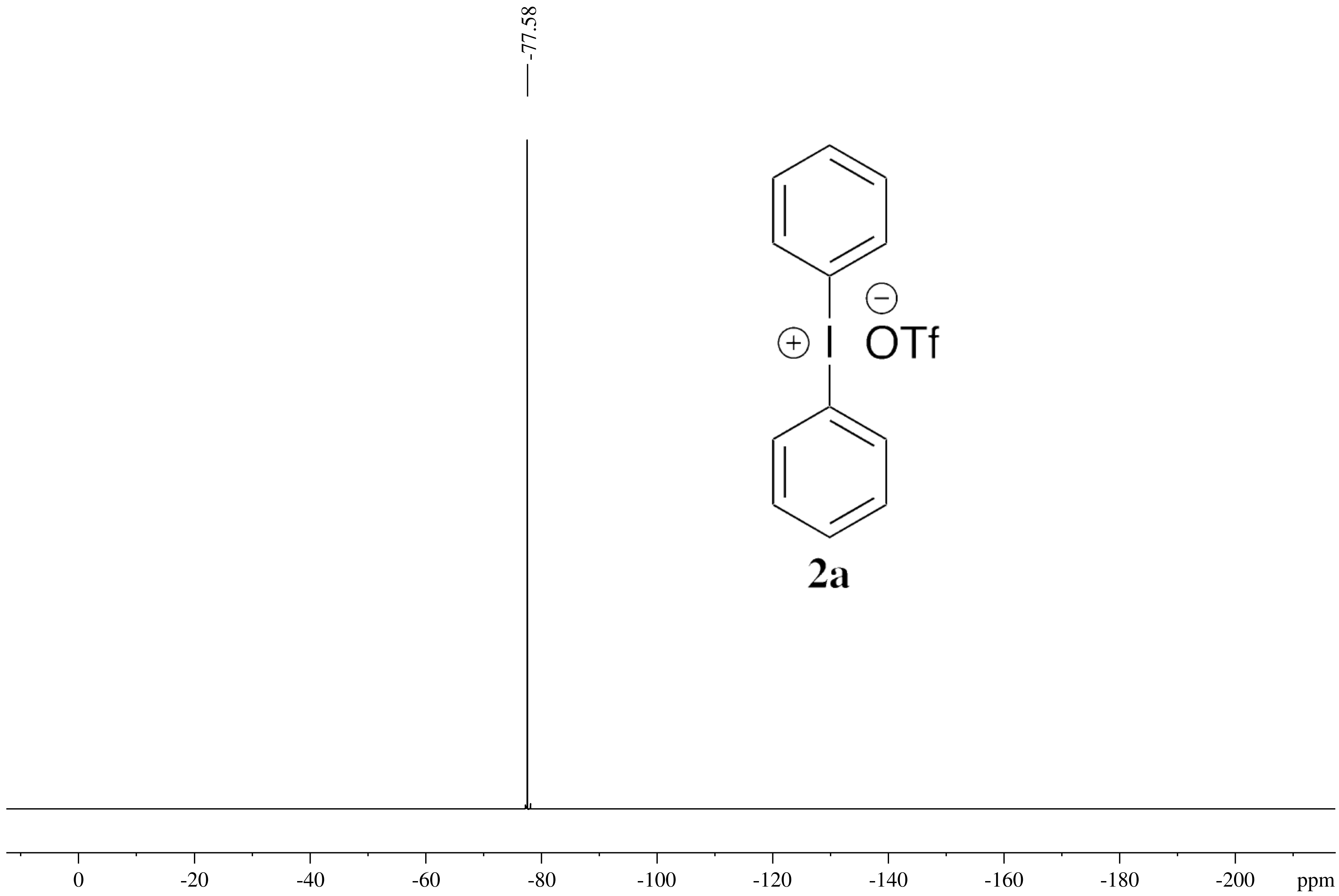


^{13}C NMR, $(CD_3)_2SO$, 100 MHz

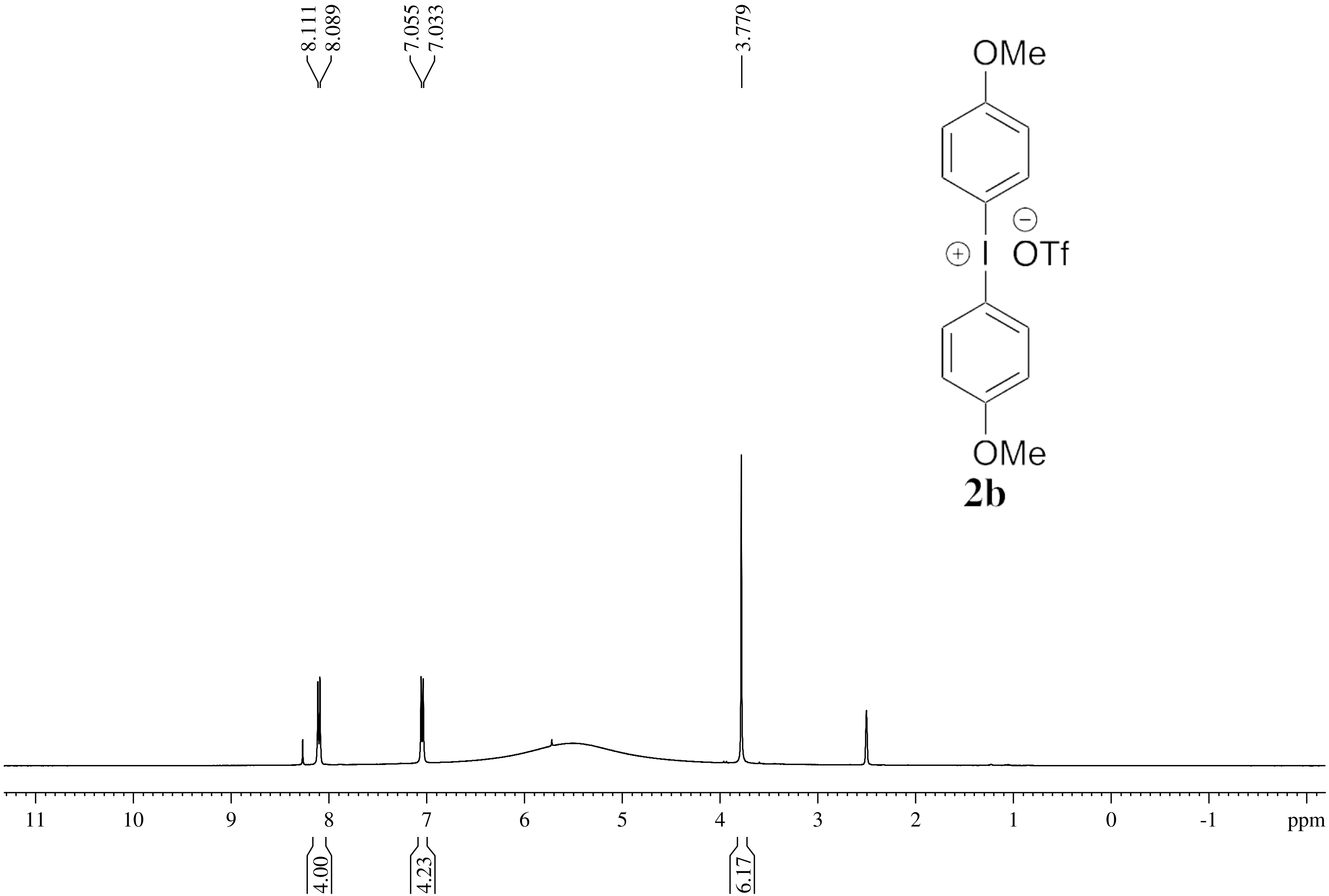


2a

^{19}F NMR, $(CD_3)_2SO$, 376 MHz

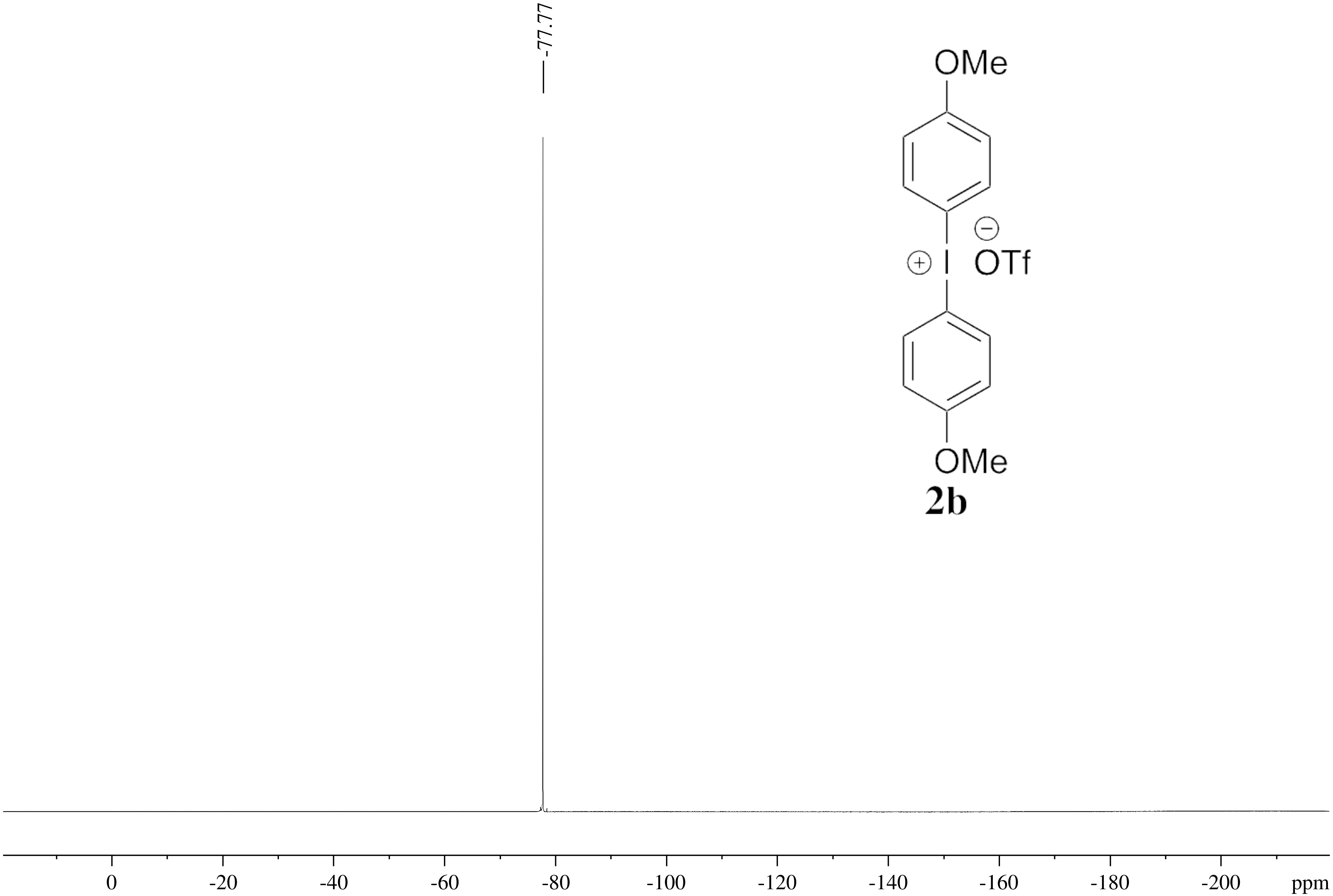


^{1}H NMR, $(CD_3)_2SO$, 400 MHz



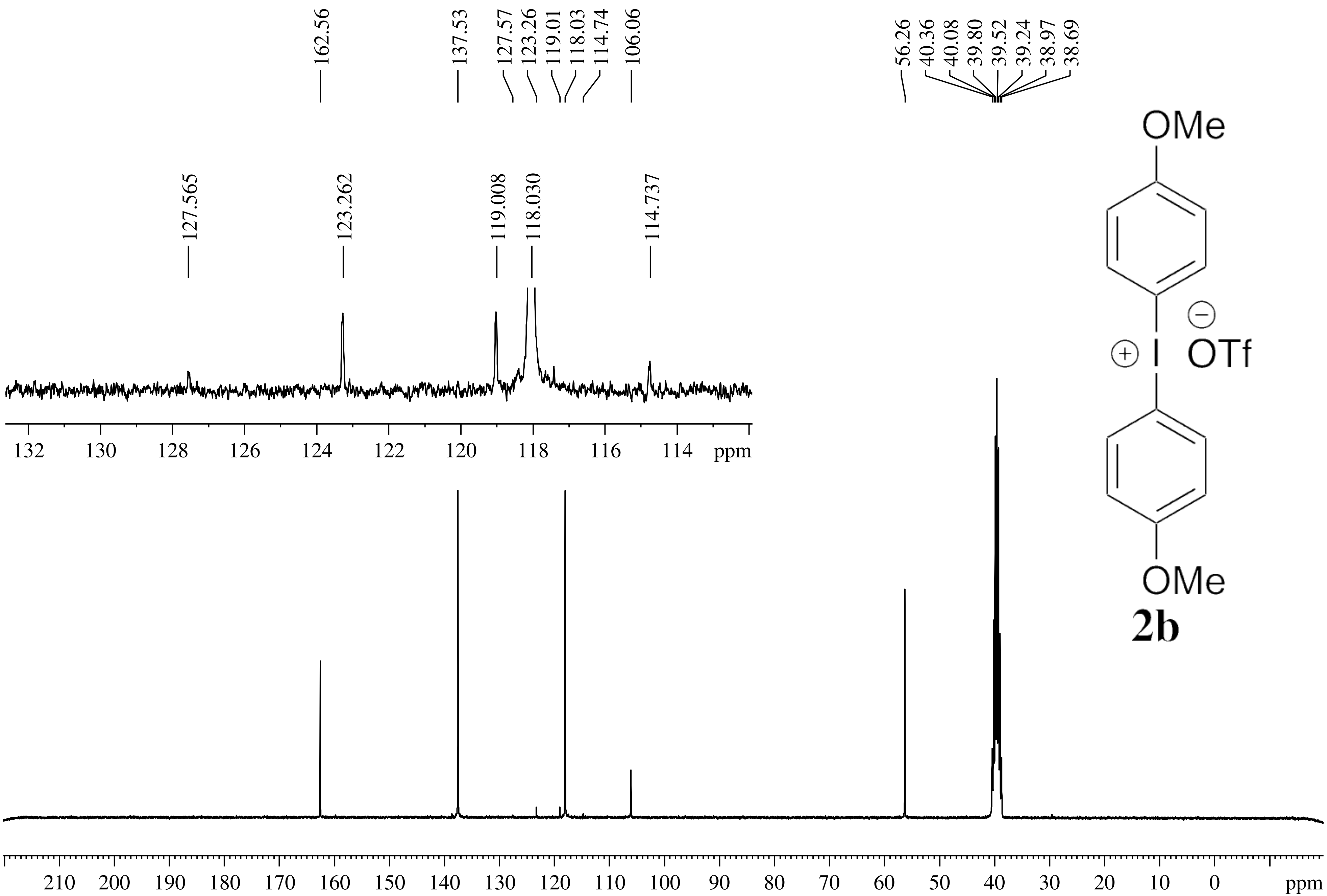
2b

^{19}F NMR, $(CD_3)_2SO$, 282 MHz



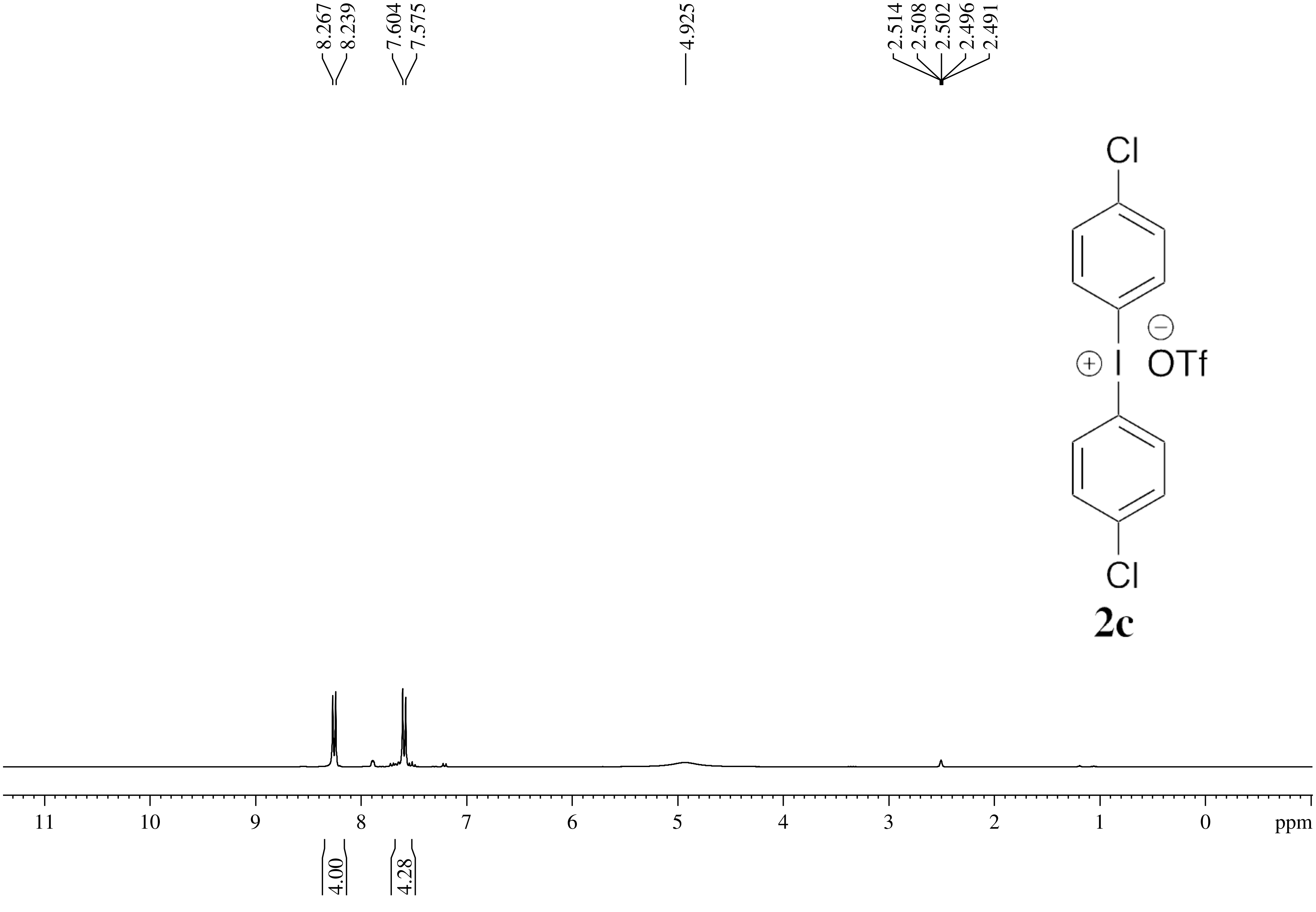
2b

^{13}C NMR, $(CD_3)_2SO$, 75 MHz



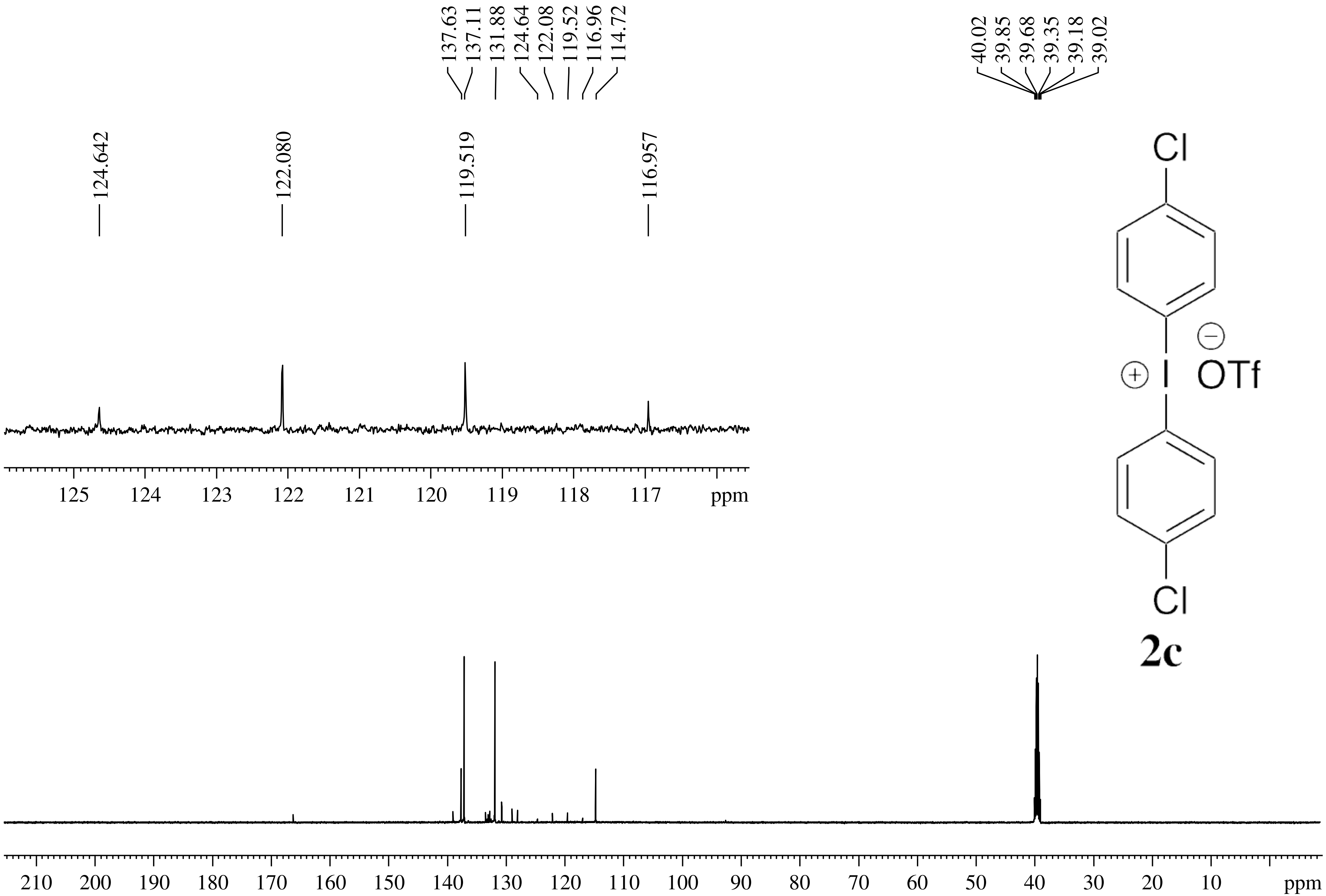
2b

¹H NMR, $(CD_3)_2SO$, 300 MHz



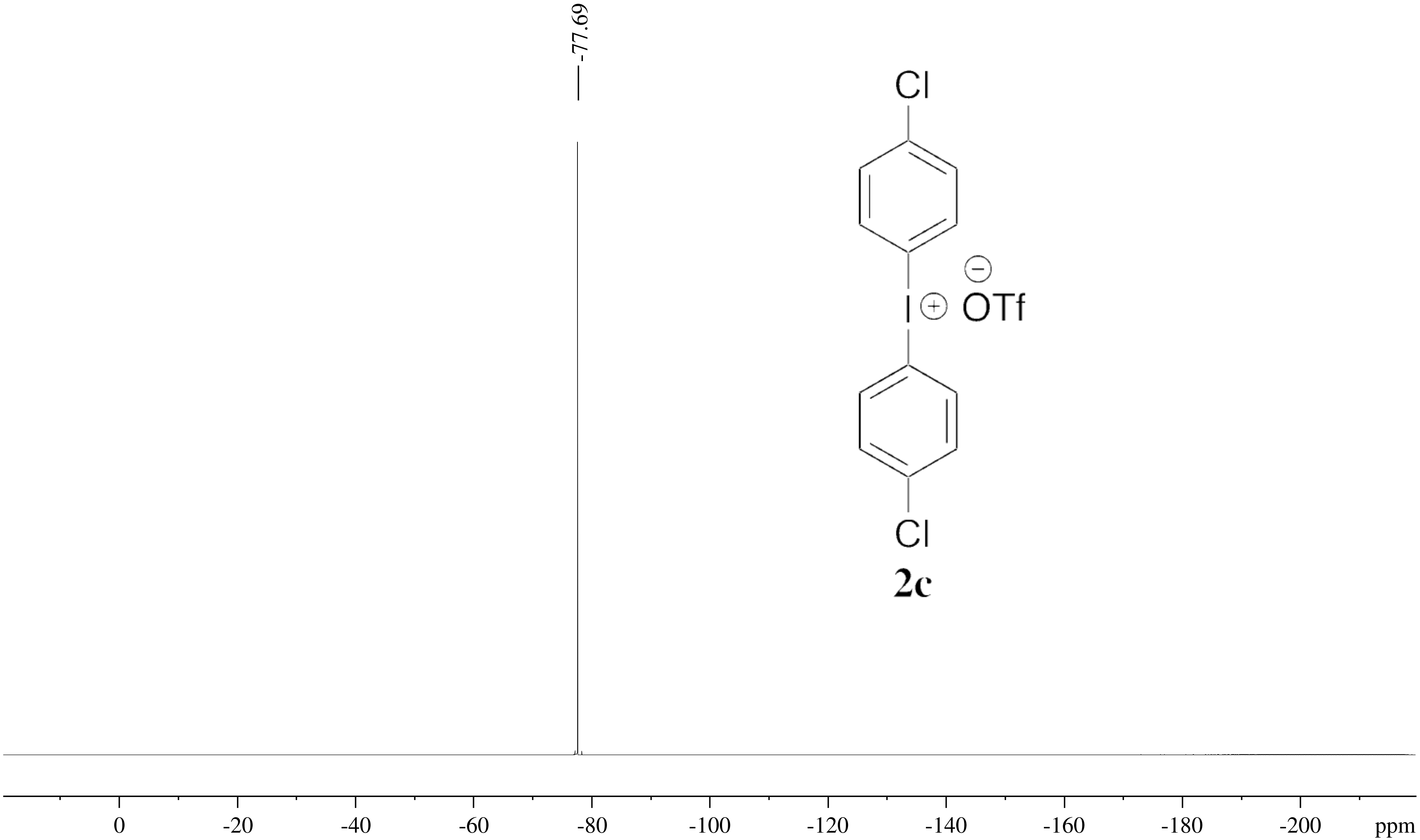
2c

^{13}C NMR, $(CD_3)_2SO$, 125 MHz



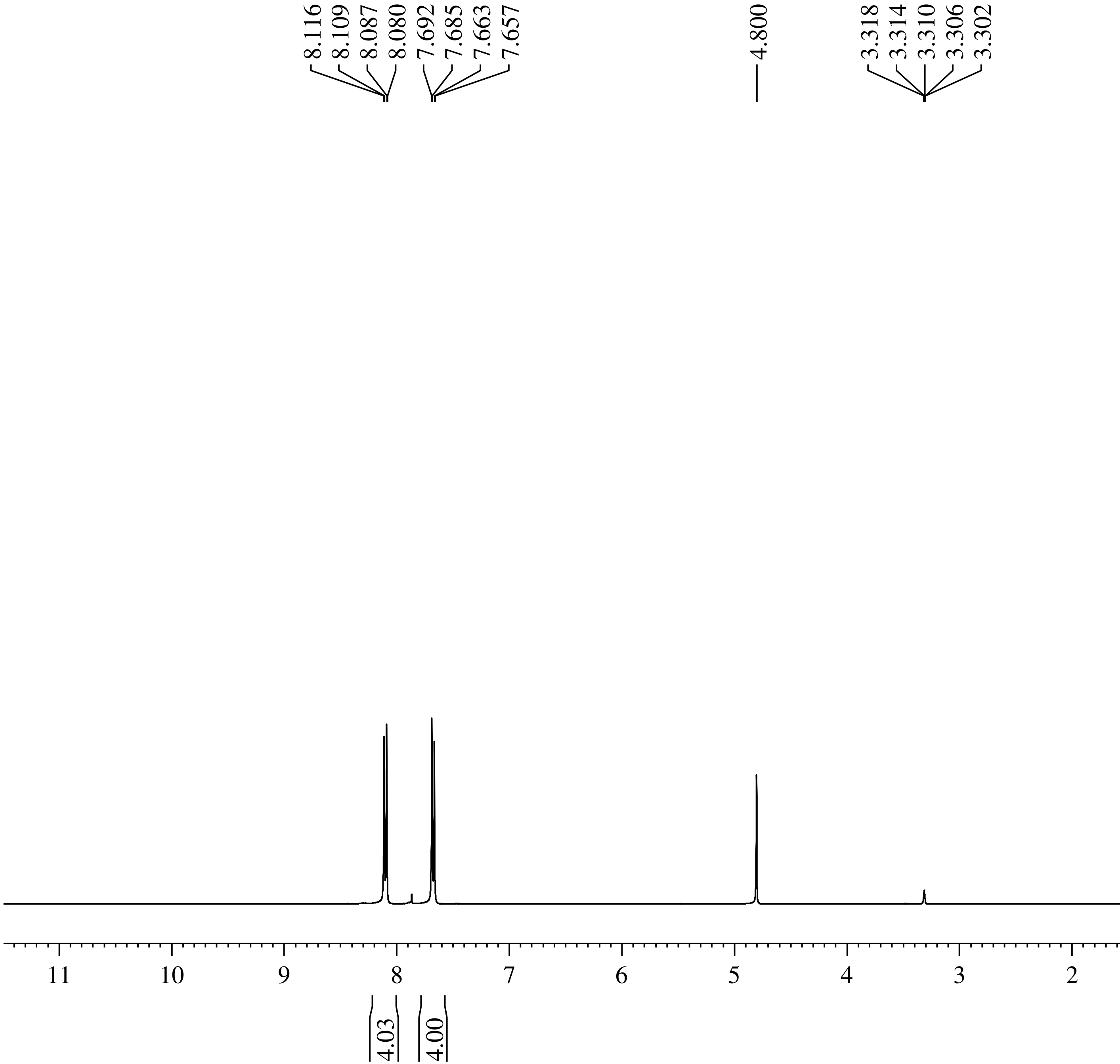
2c

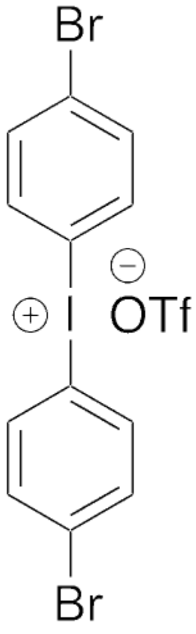
^{19}F NMR, $(CD_3)_2SO$, 282 MHz



2c

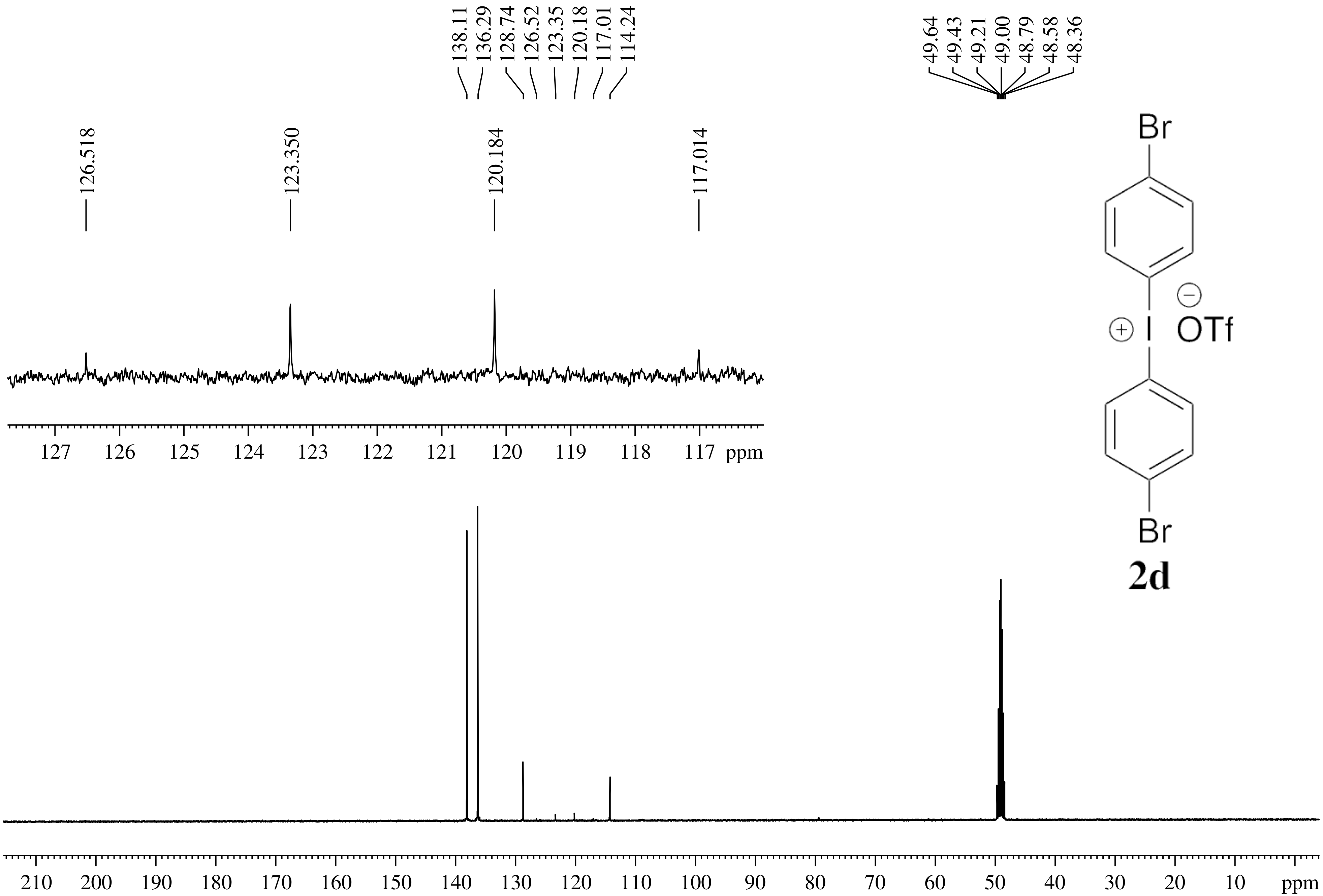
^{1}H NMR, $(CD_3)_2SO$, 400 MHz





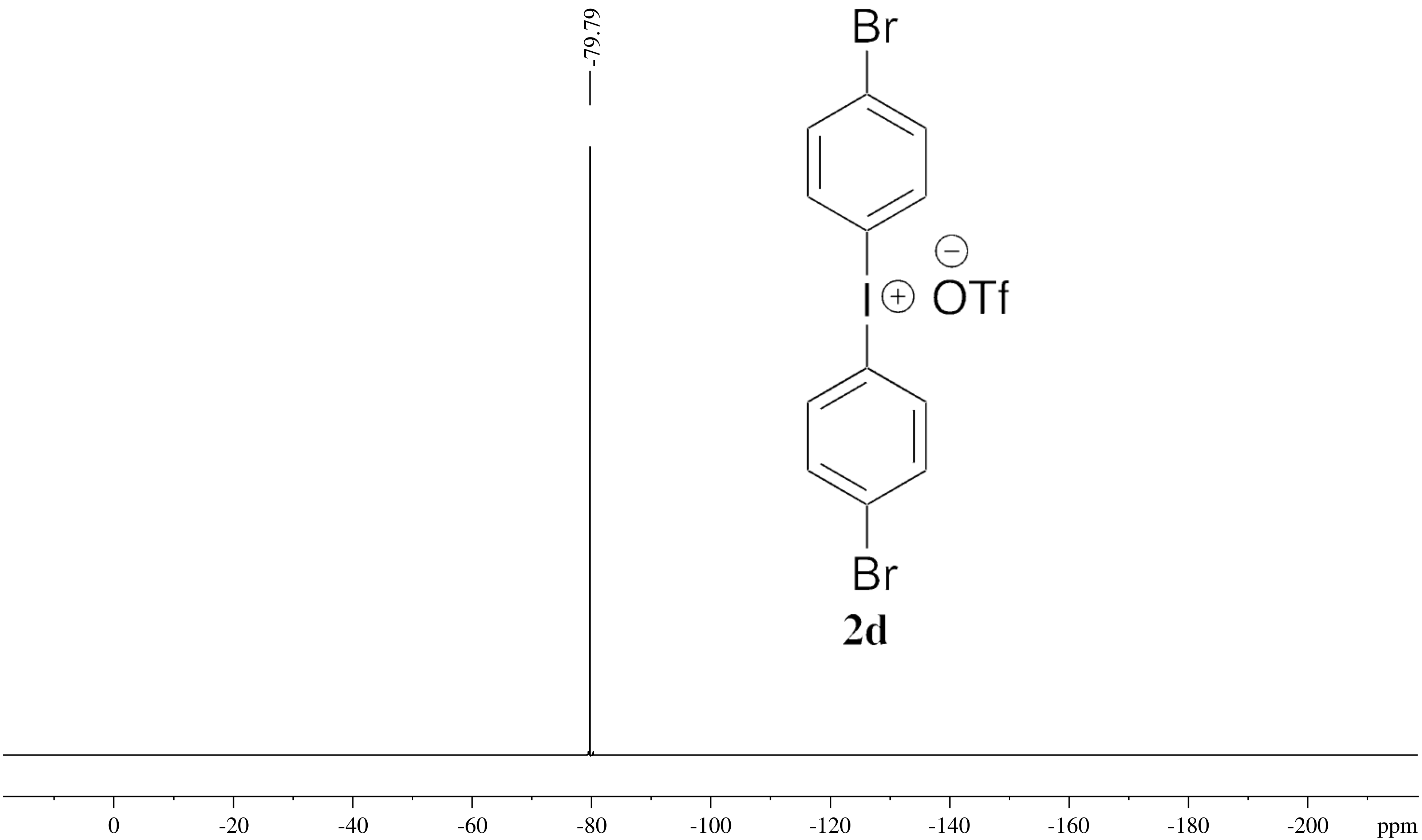
2d

^{13}C NMR, $(CD_3)_2SO$, 100 MHz

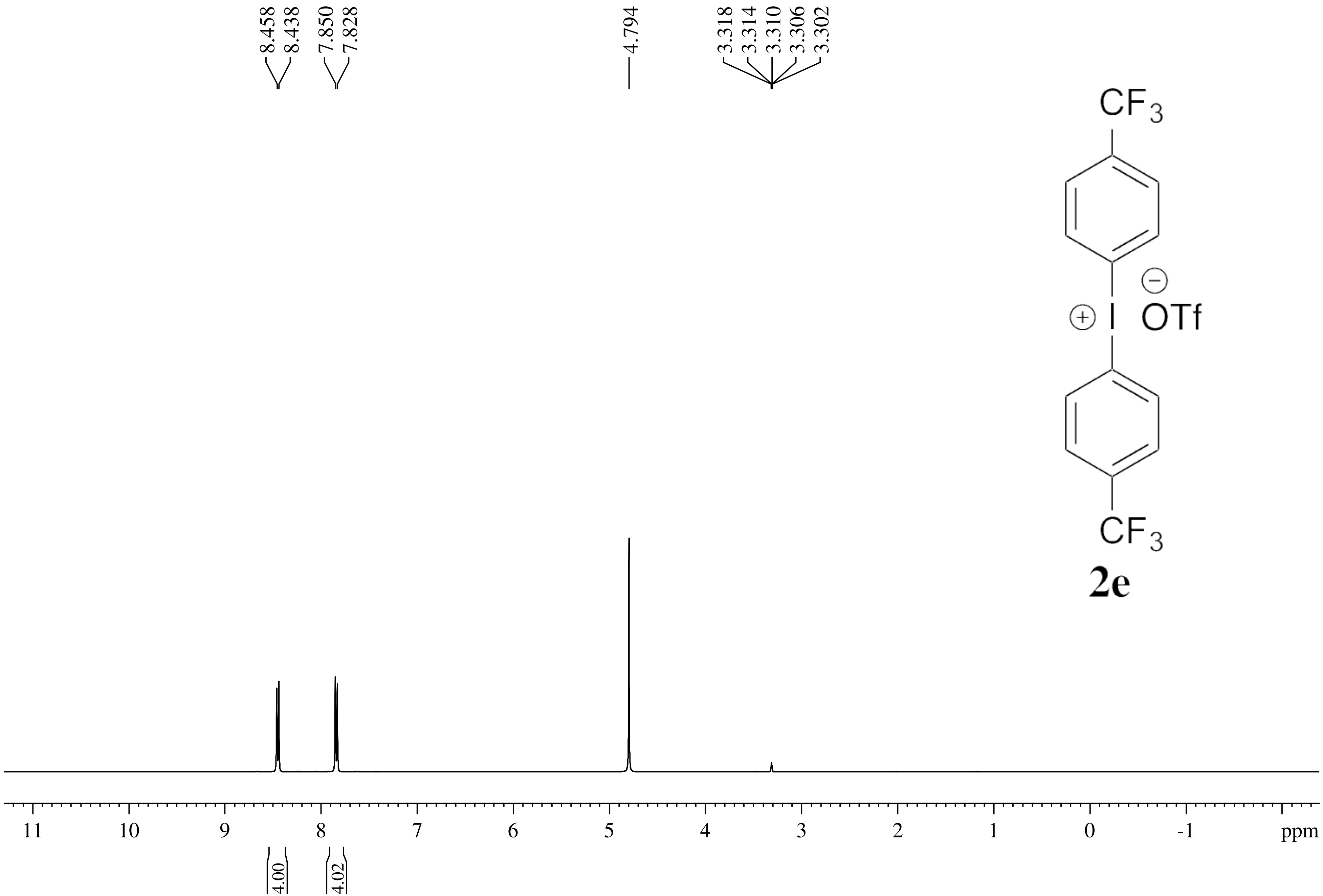


2d

^{19}F NMR, $(CD_3)_2SO$, 376 MHz

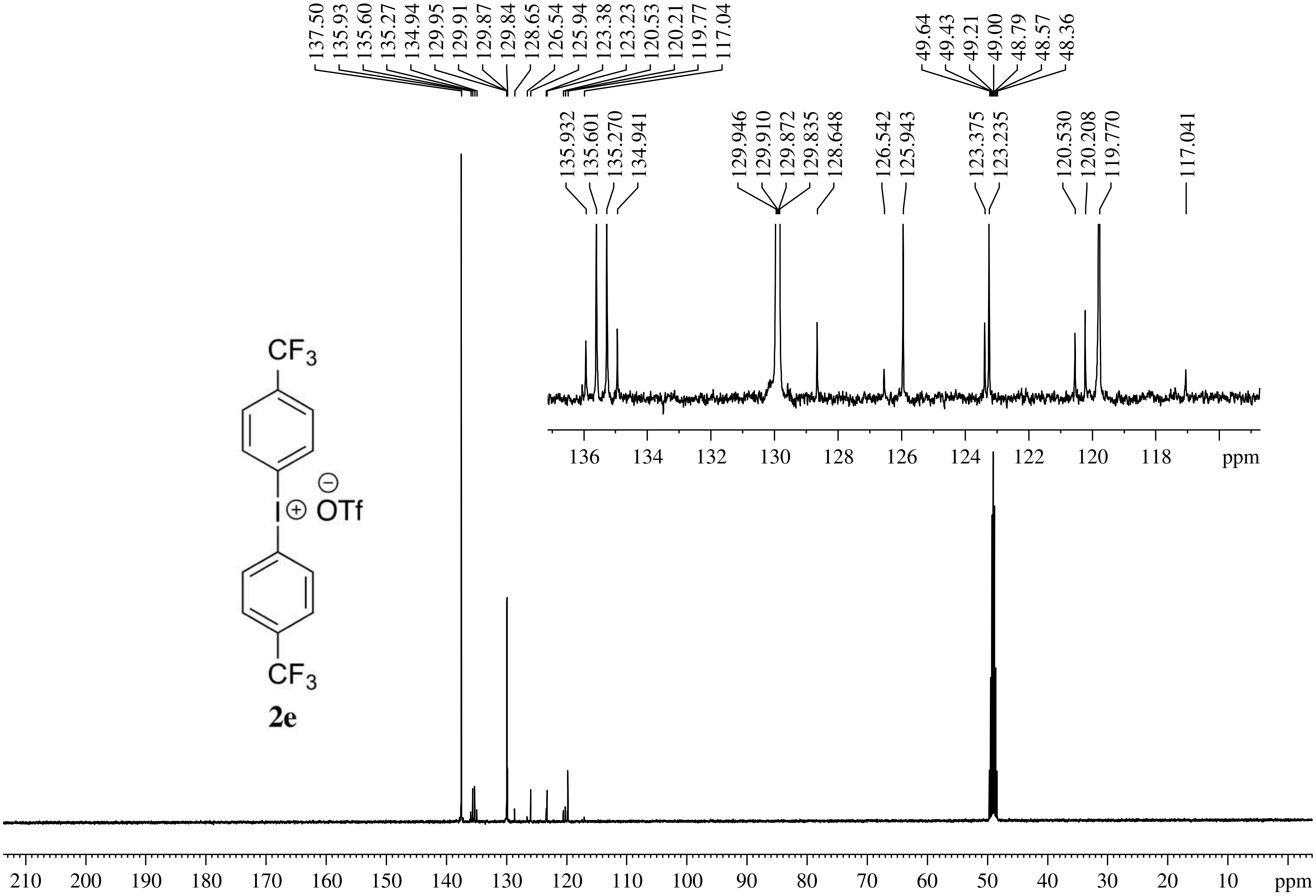


^1H NMR, CD_3OD, 400 MHz

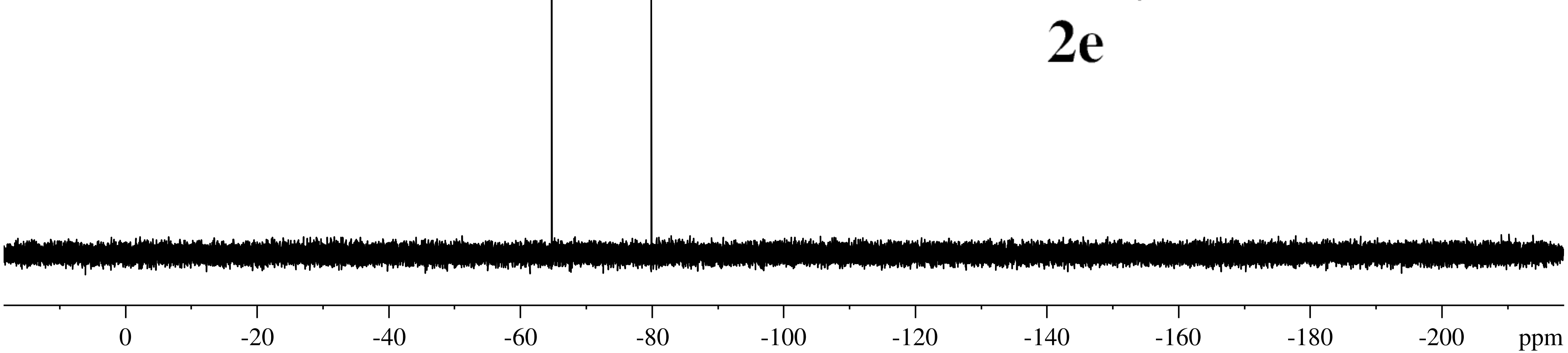


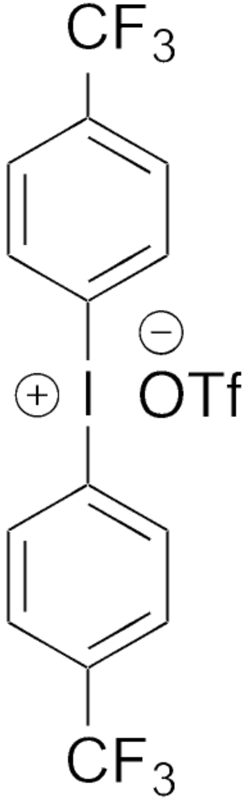
2e

^{13}C NMR, CD_3OD, 100 MHz

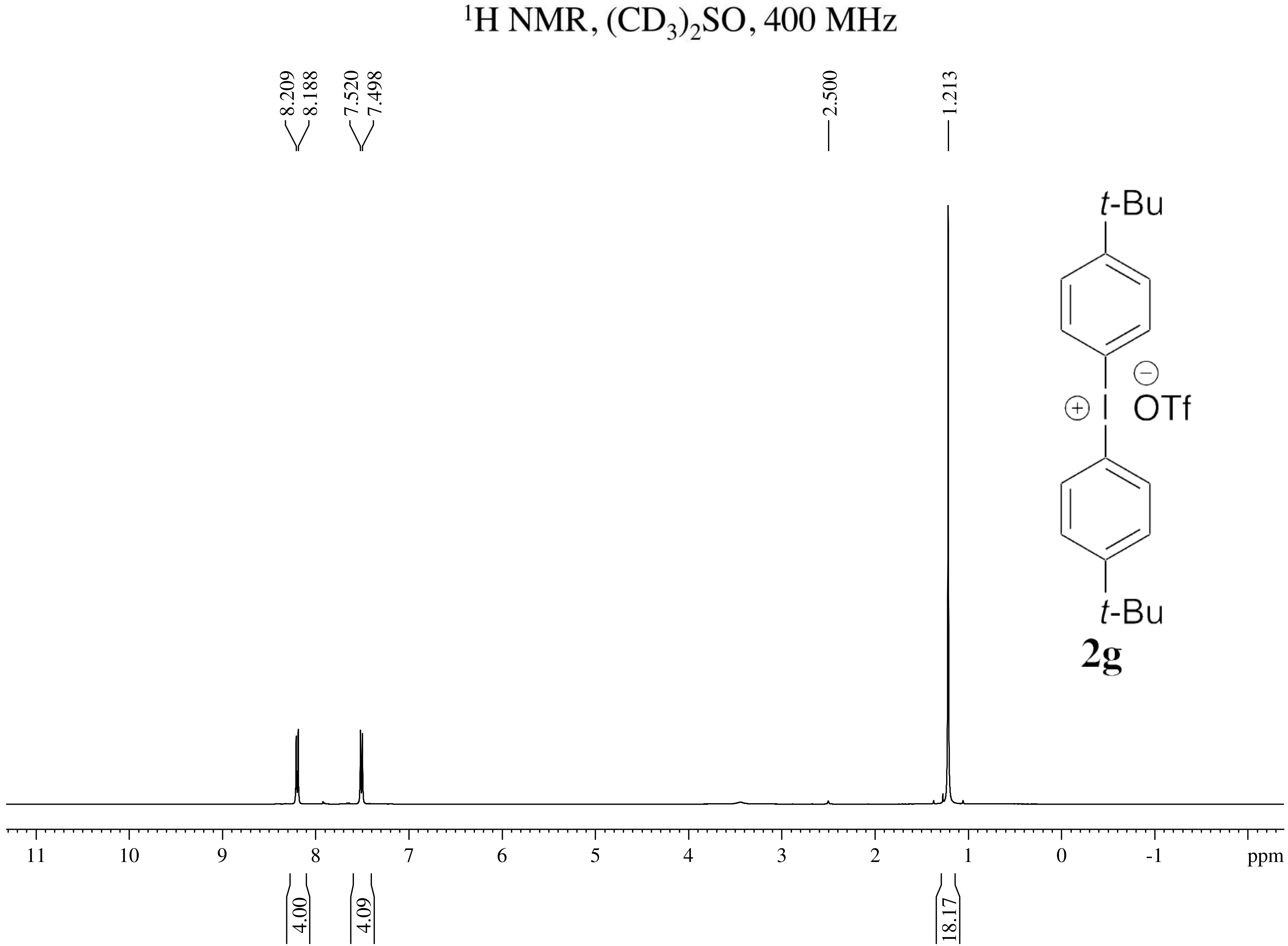


^{19}F NMR, CD_3OD, 376 MHz





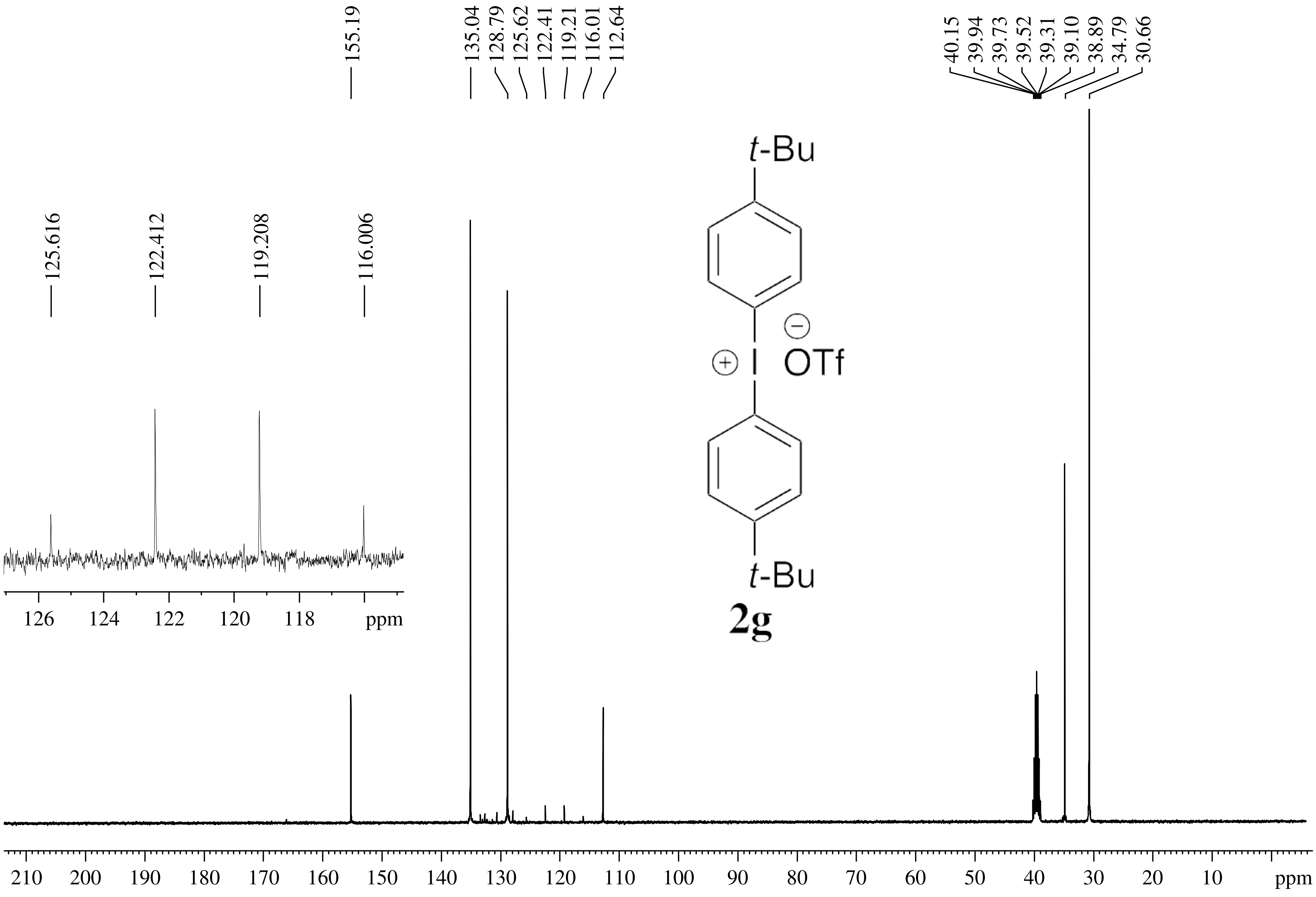
2e



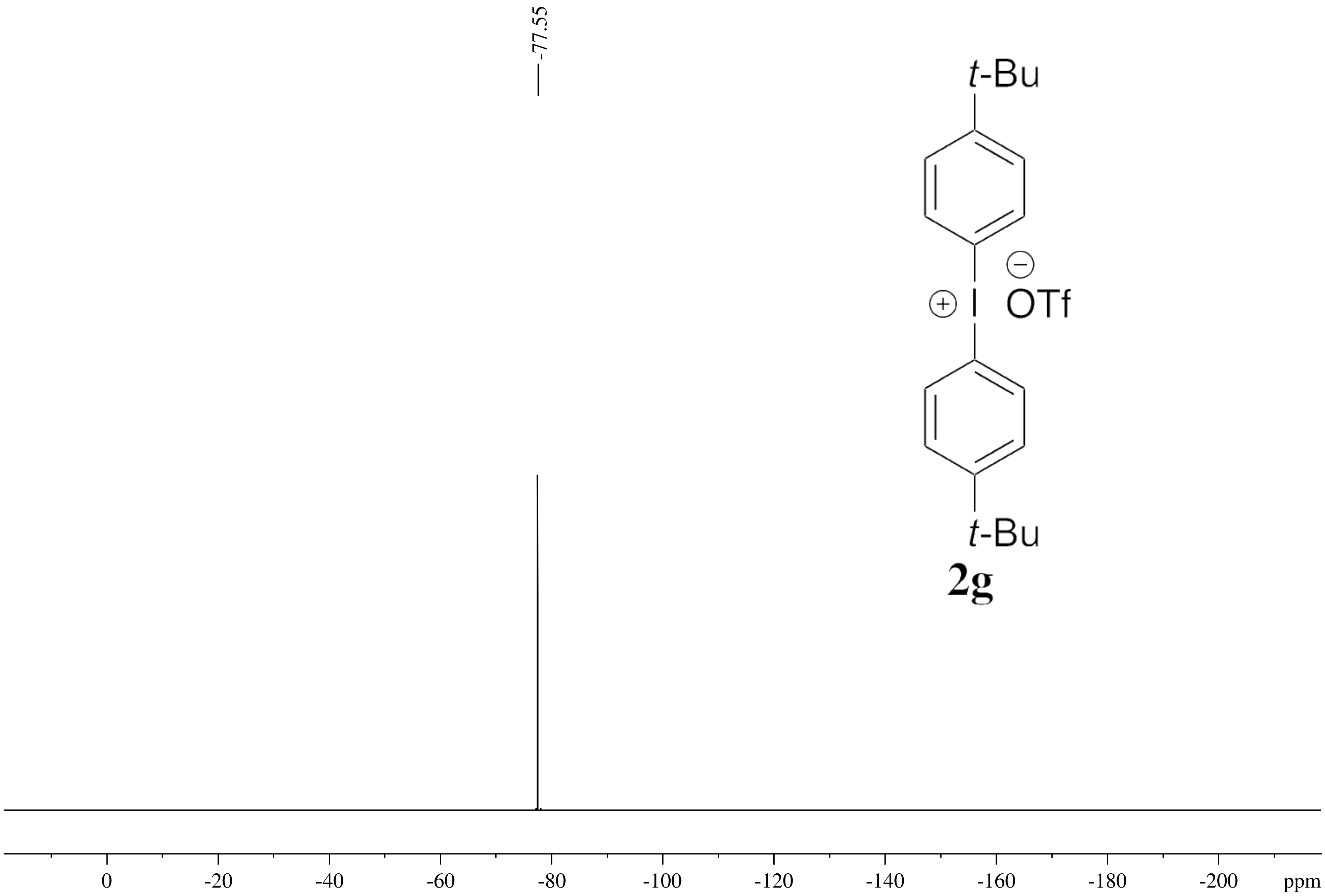
^1H NMR, $(CD_3)_2SO$, 400 MHz
8.209
8.188
7.520
7.498
2.500
1.213
t-Bu
OTf
t-Bu
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
4.00
4.09
18.17

2g

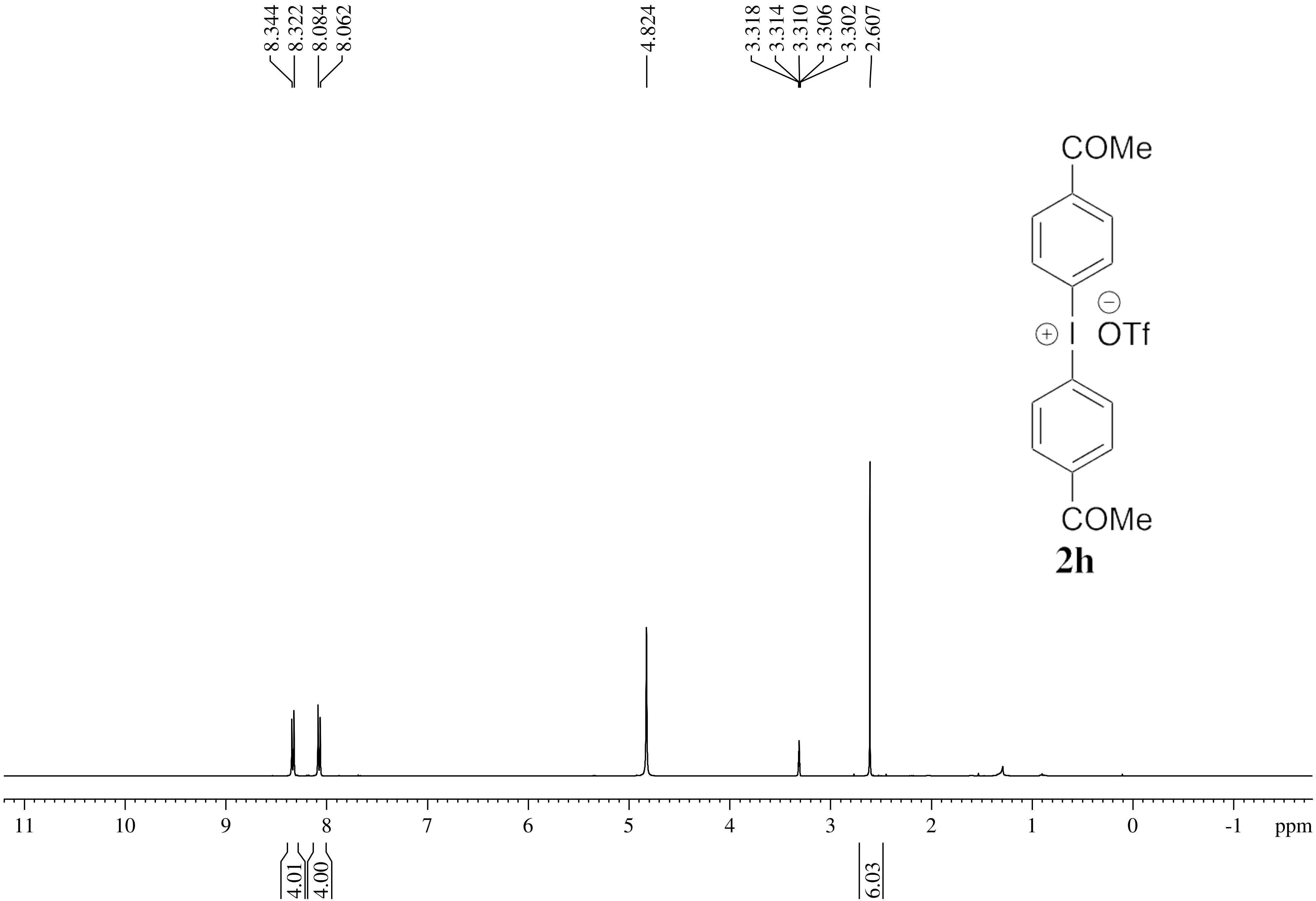
^{13}C NMR, $(CD_3)_2SO$, 125 MHz



19F, 376 MHz, (CD3)2SO

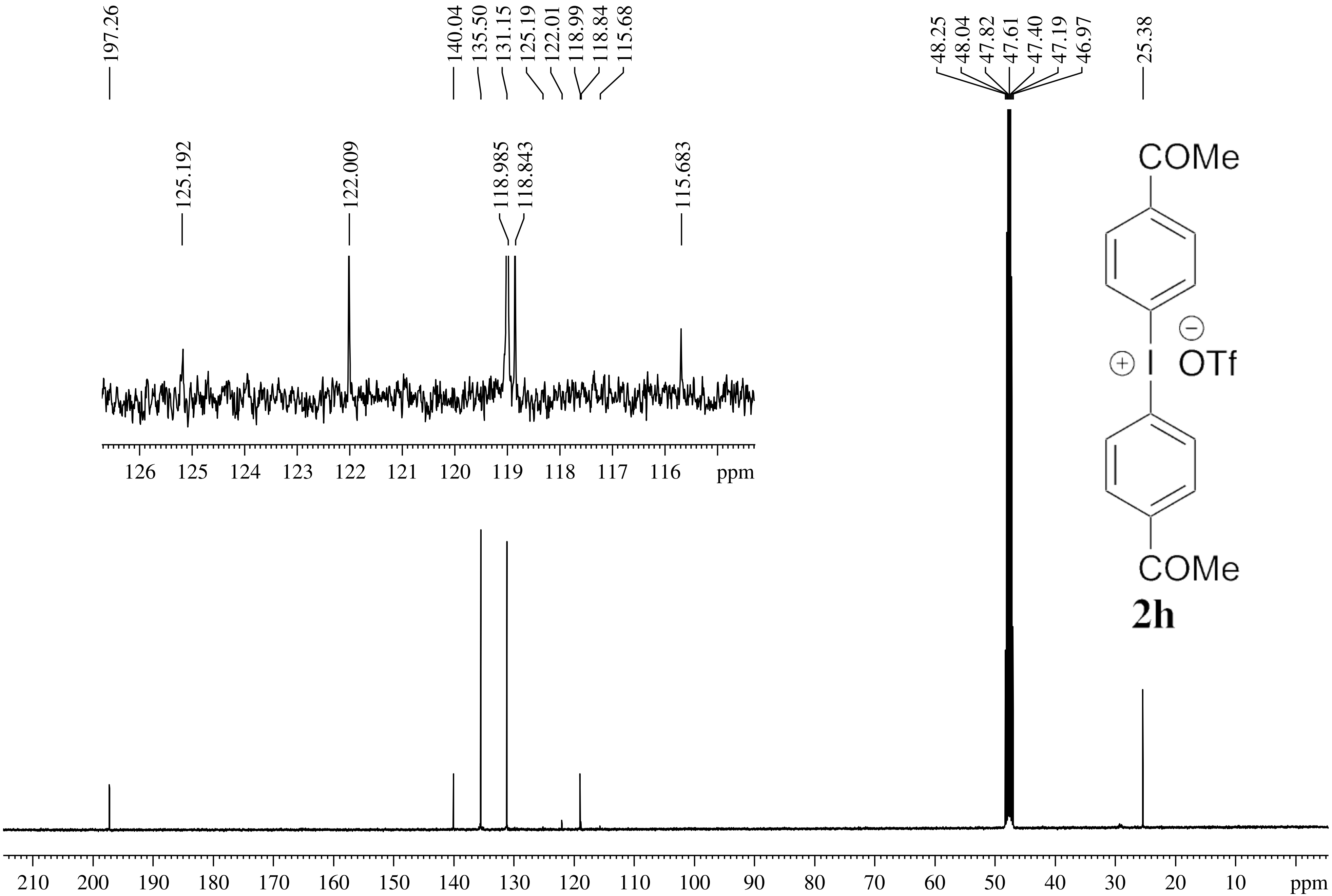


1H NMR, 400 MHz, CD3OD



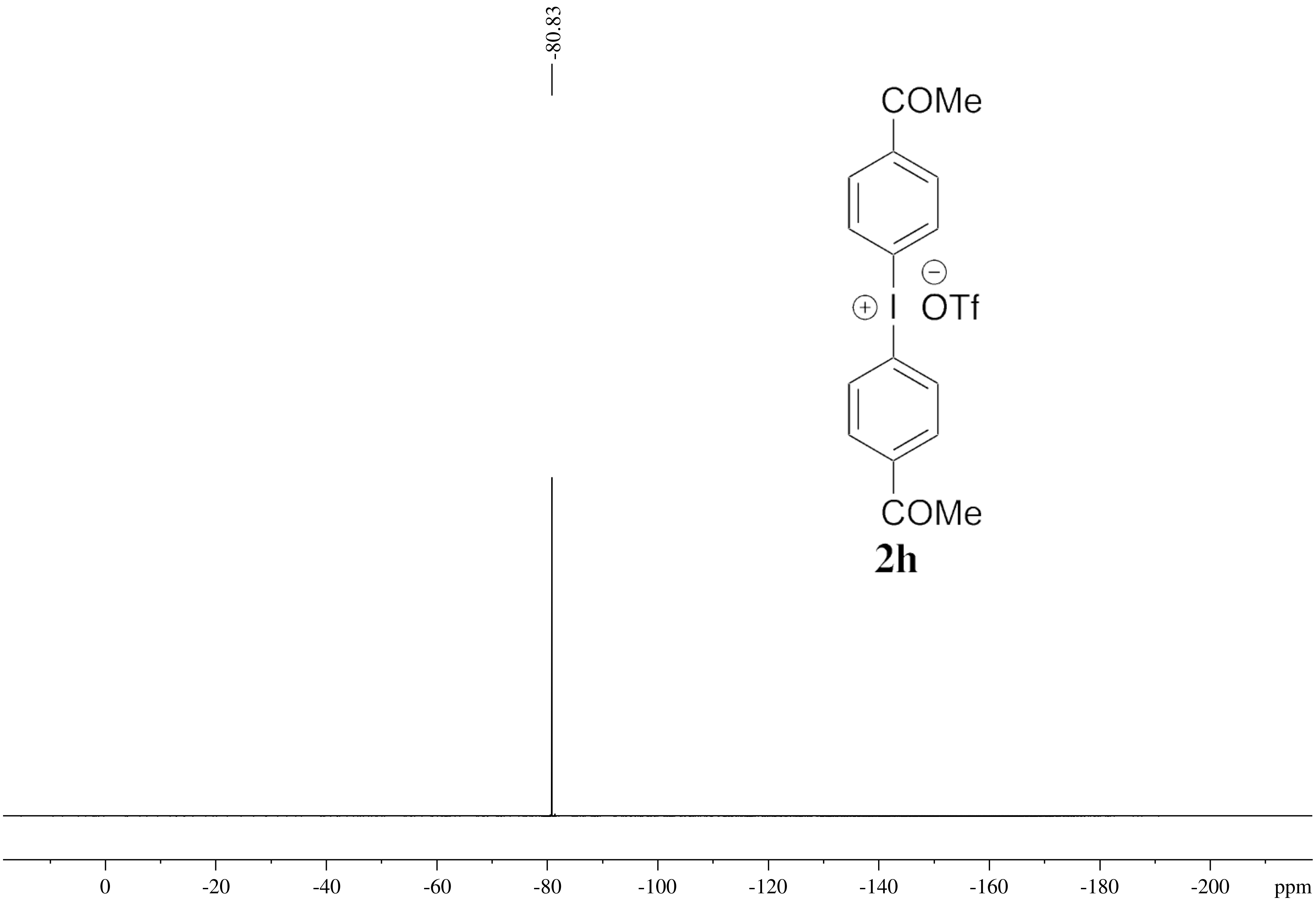
2h

13C NMR, CD3OD, 100 MHz



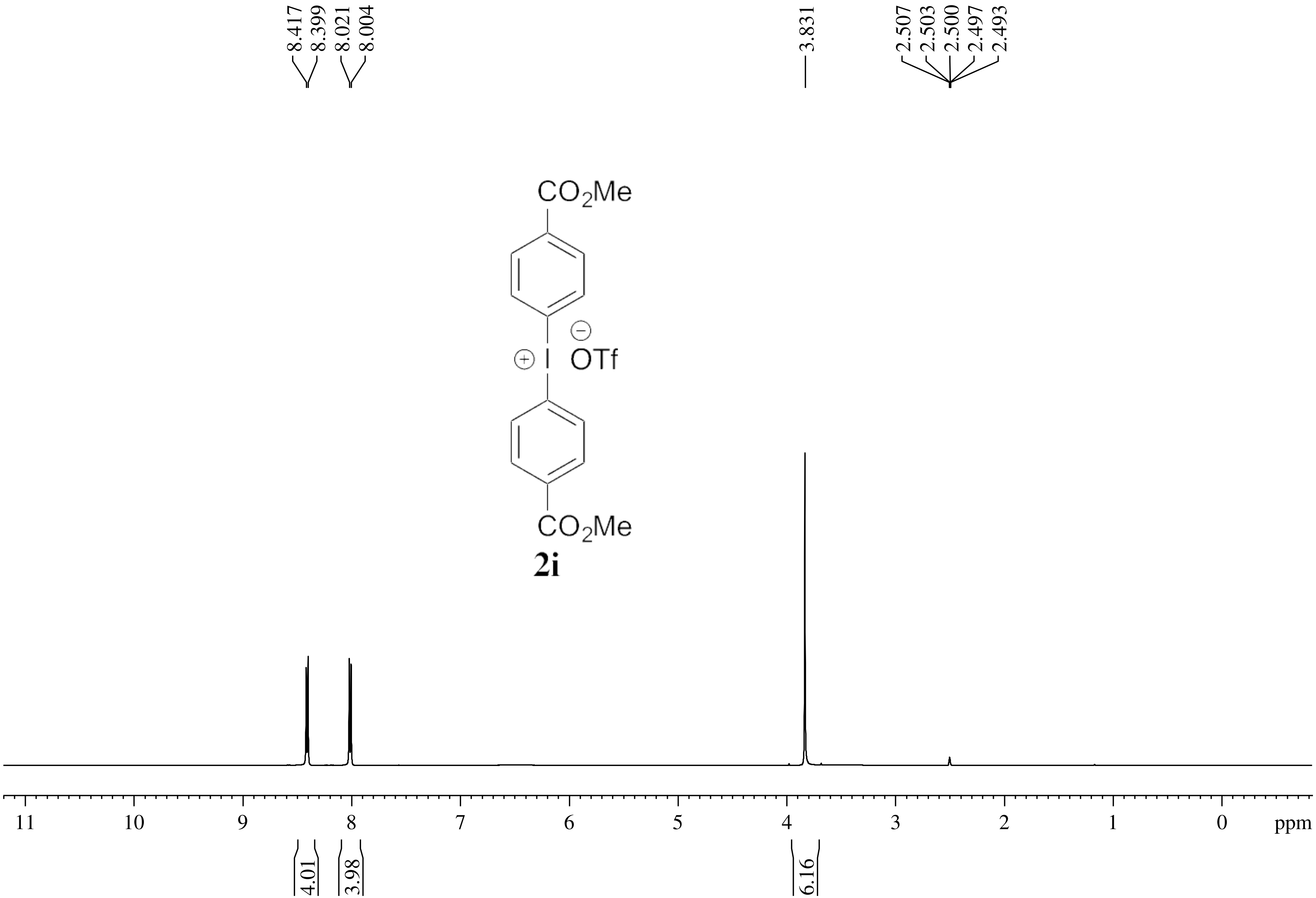
2h

19F NMR, CD3OD, 376 MHz



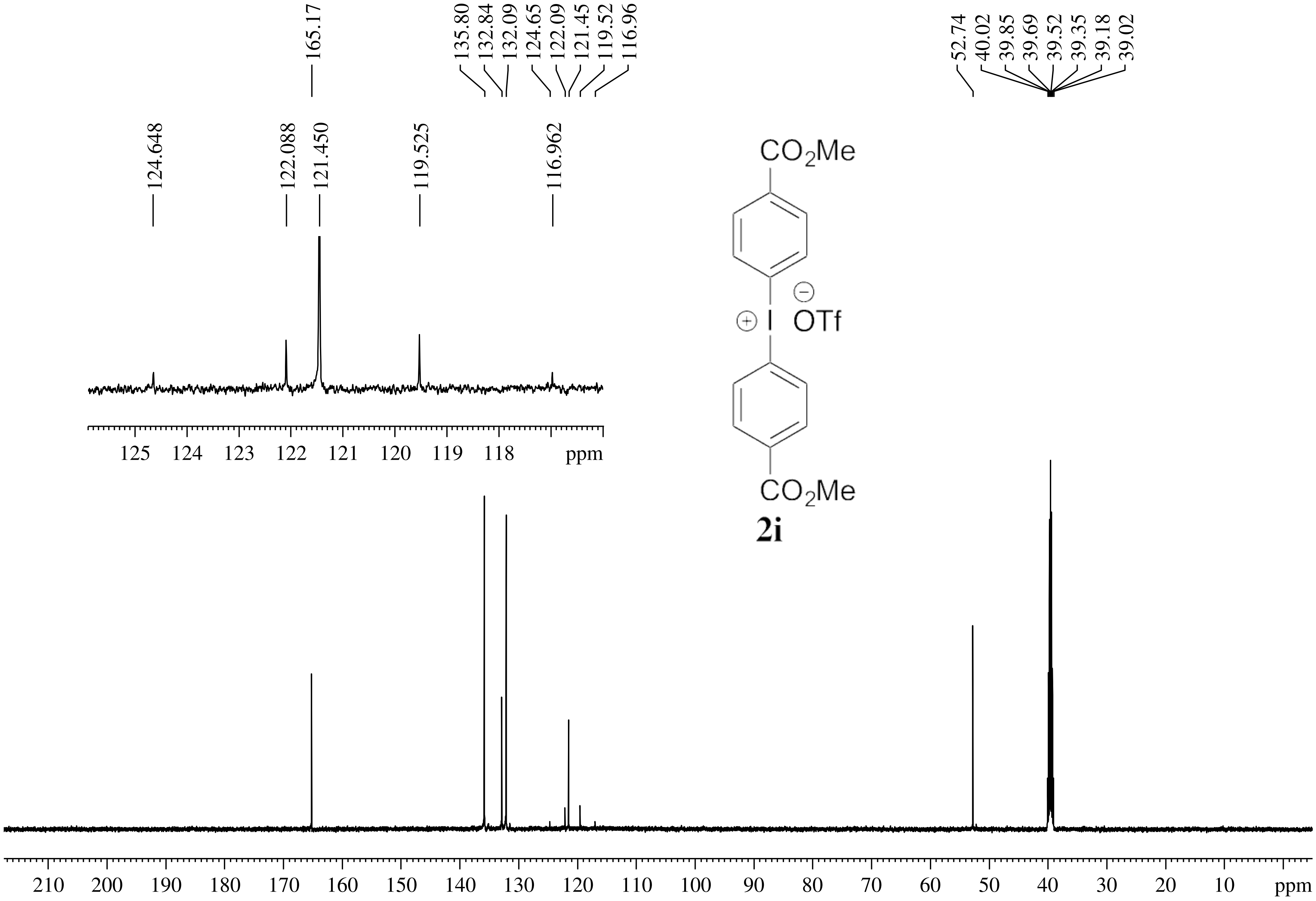
2h

1H NMR, (CD3)2SO, 500 MHz



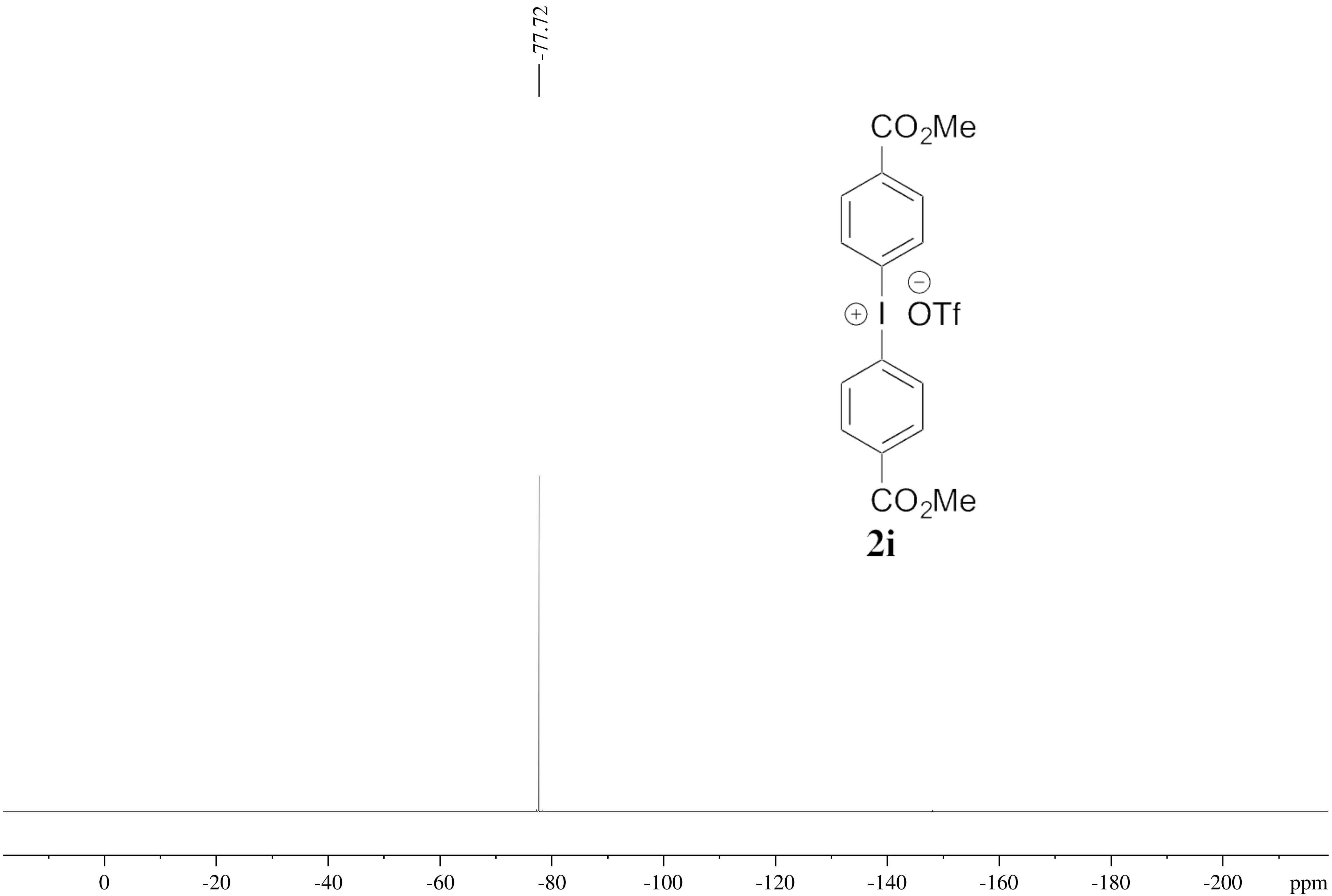
2i

13C NMR, 125 MHz, (CD3)2SO

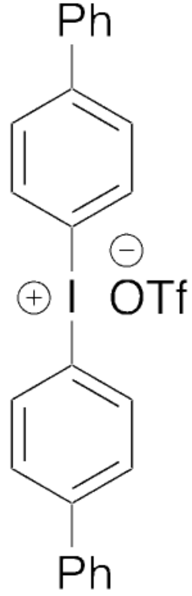


2i

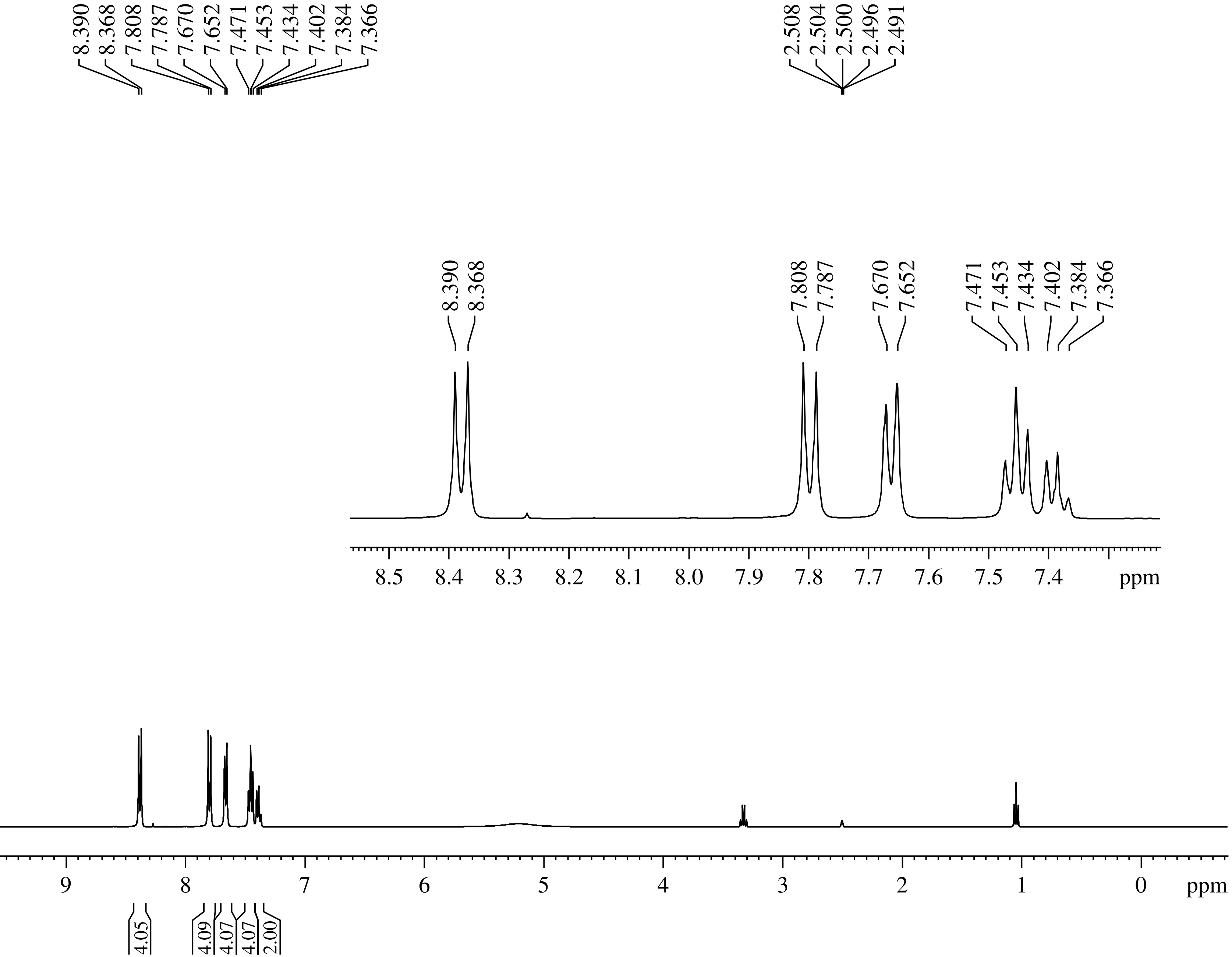
19F NMR, (CD3)2SO, 282 MHz



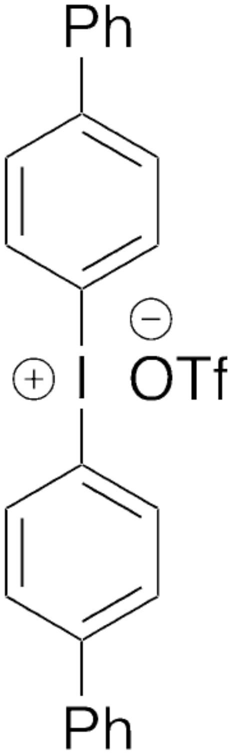
1H NMR, (CD3)2SO, 400 MHz



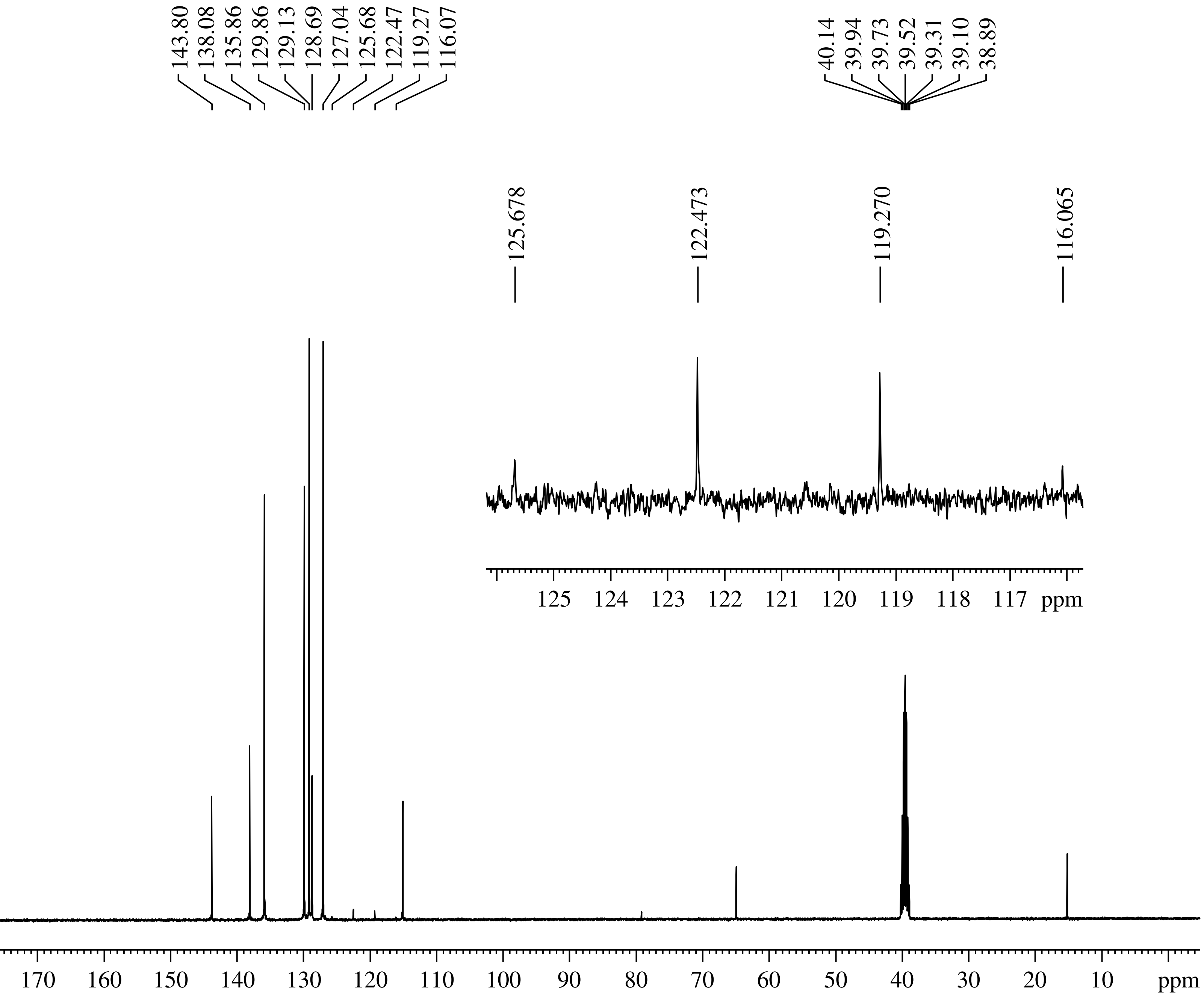
2j



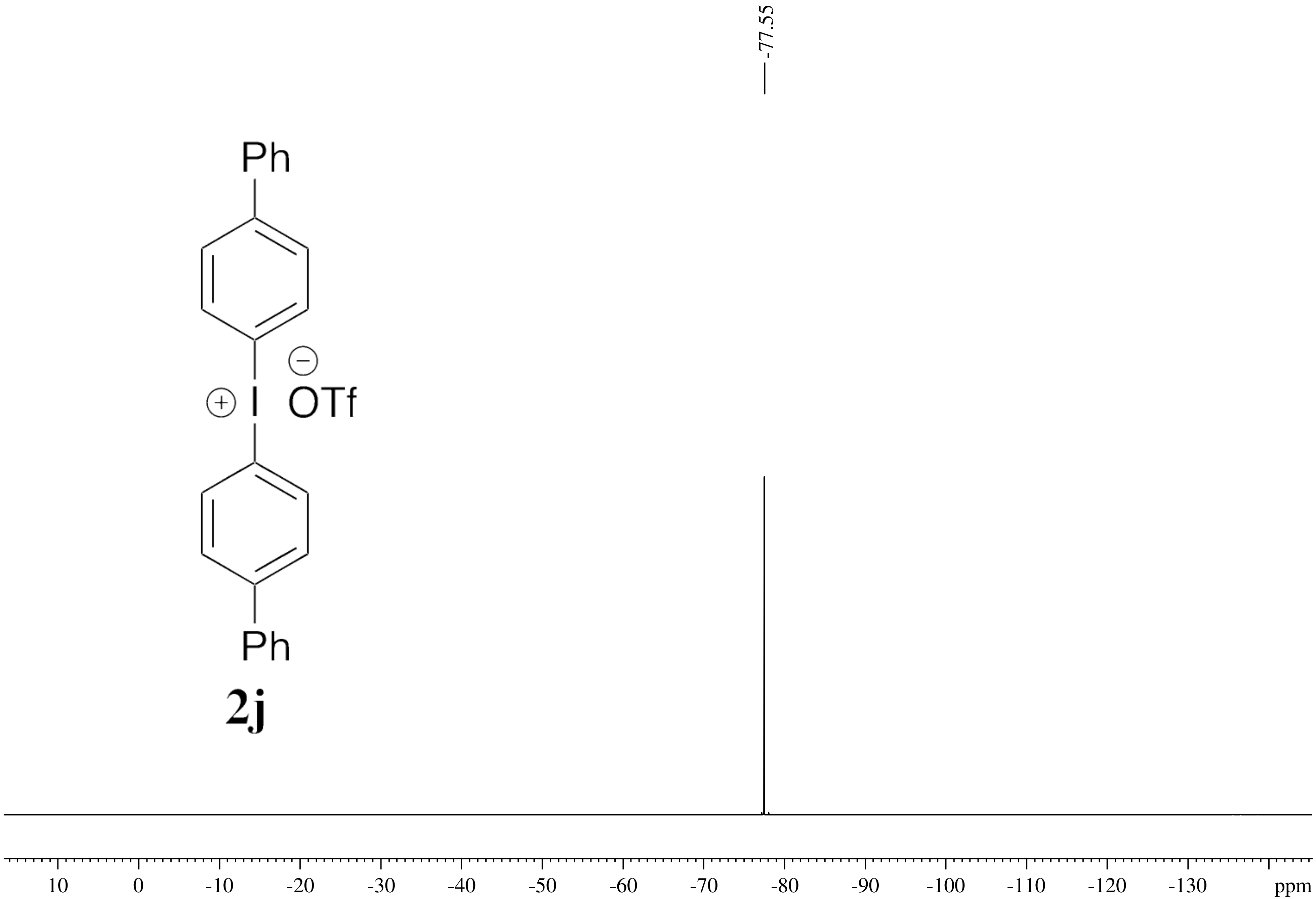
13C NMR, (CD3)2SO, 100 MHz



2j

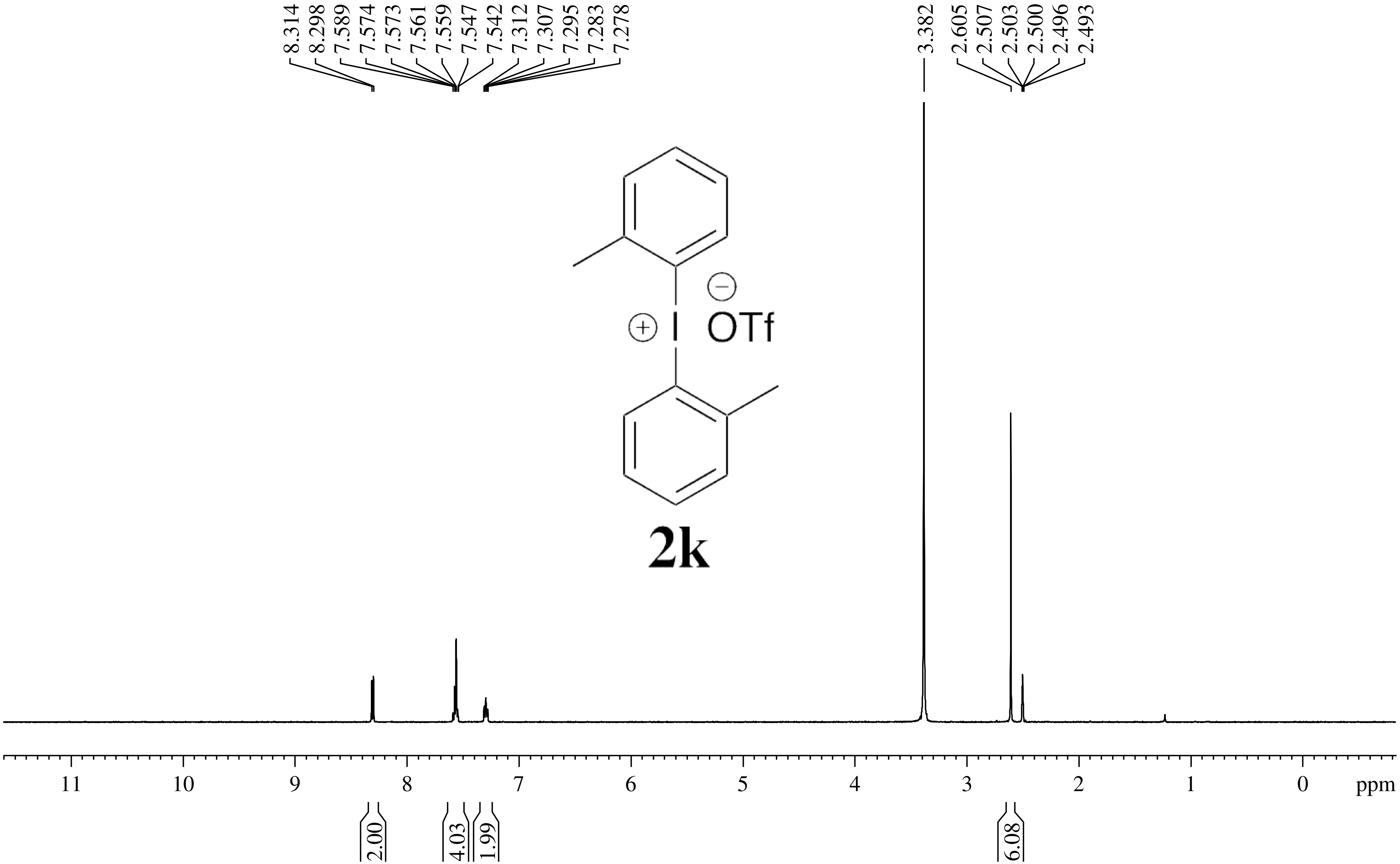


19F NMR, (CD3)2SO, 376 MHz

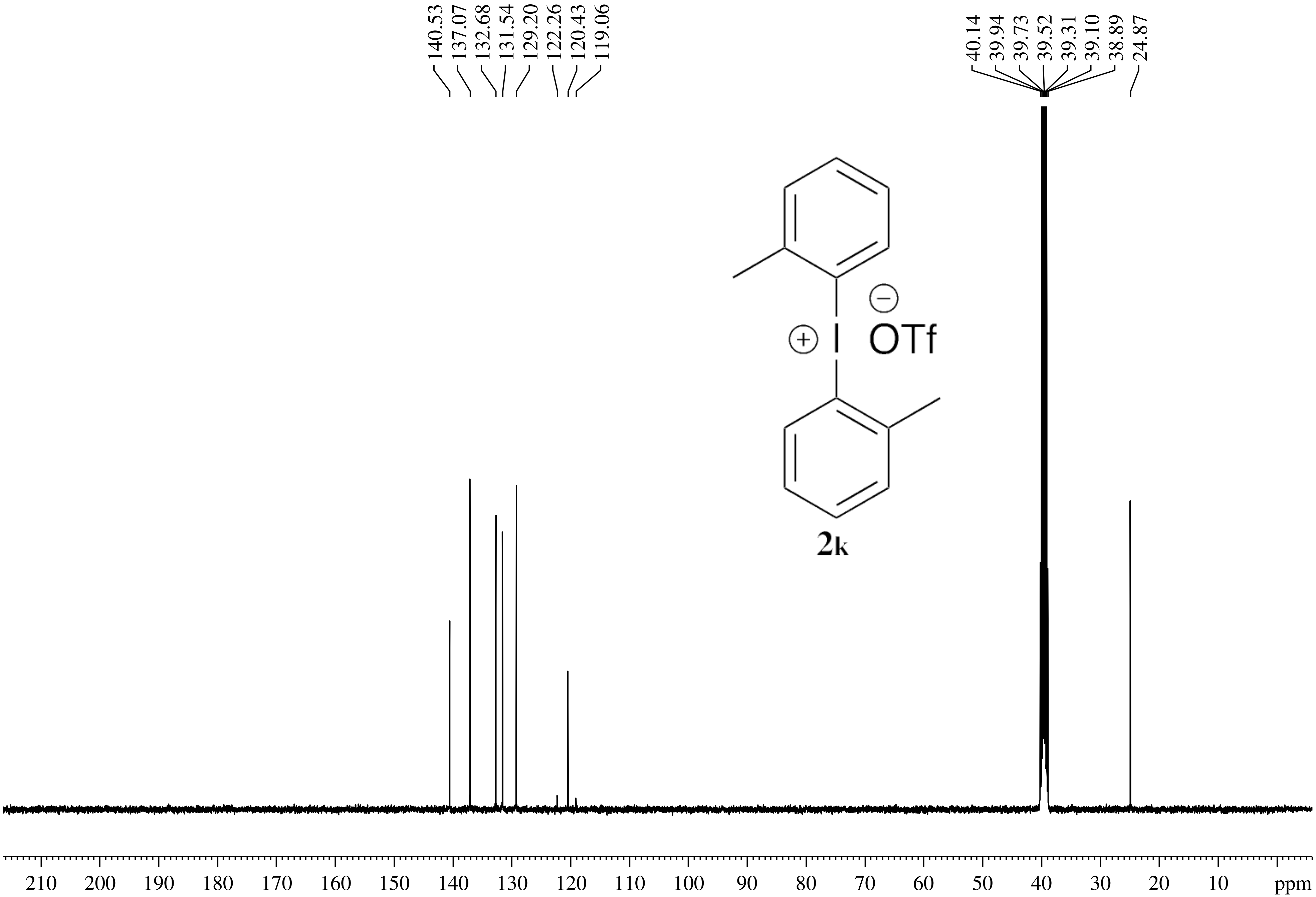


2j

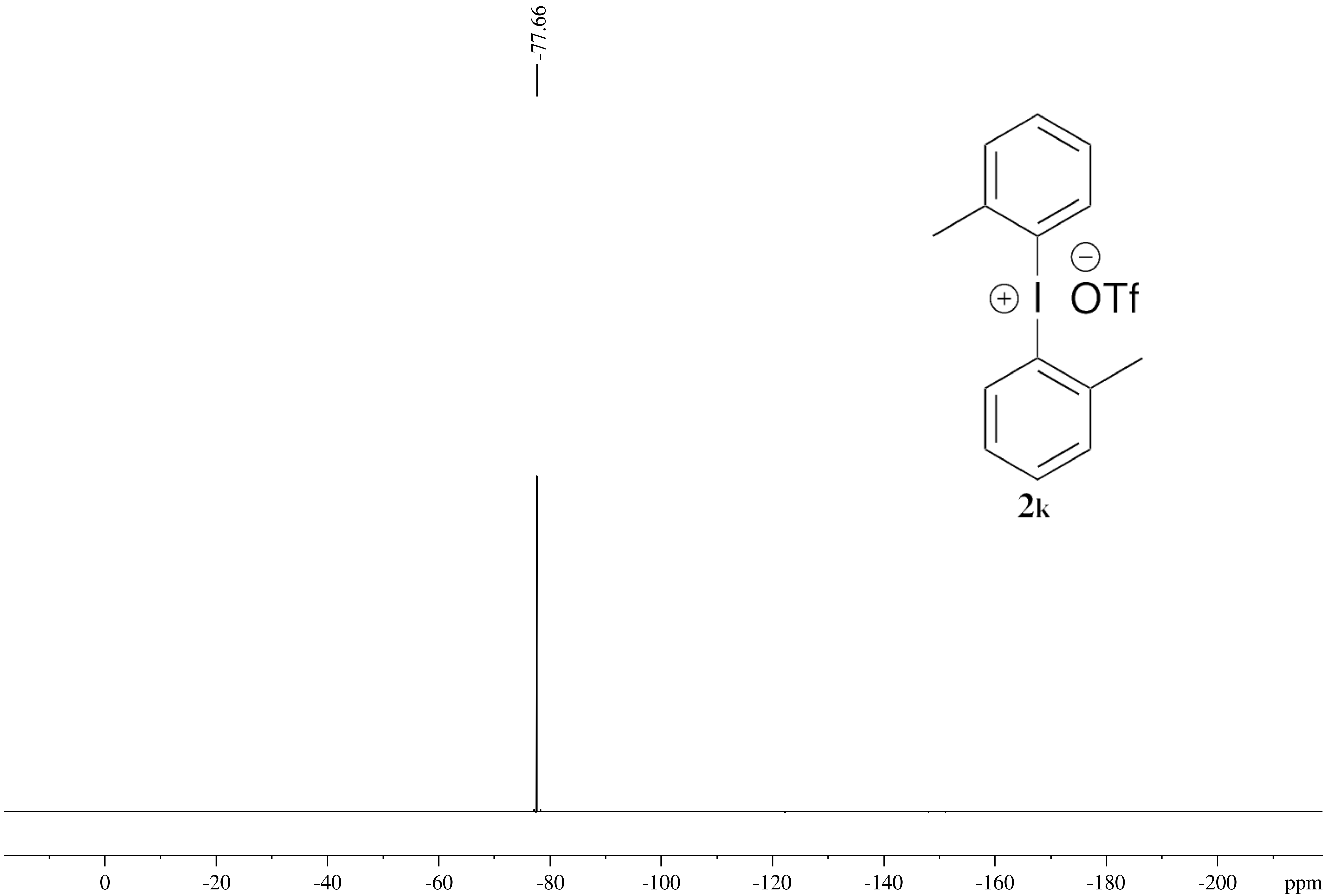
^1H NMR, $(CD_3)_2SO$, 500 MHz



13C NMR, (CD3)2SO, 100 MHz

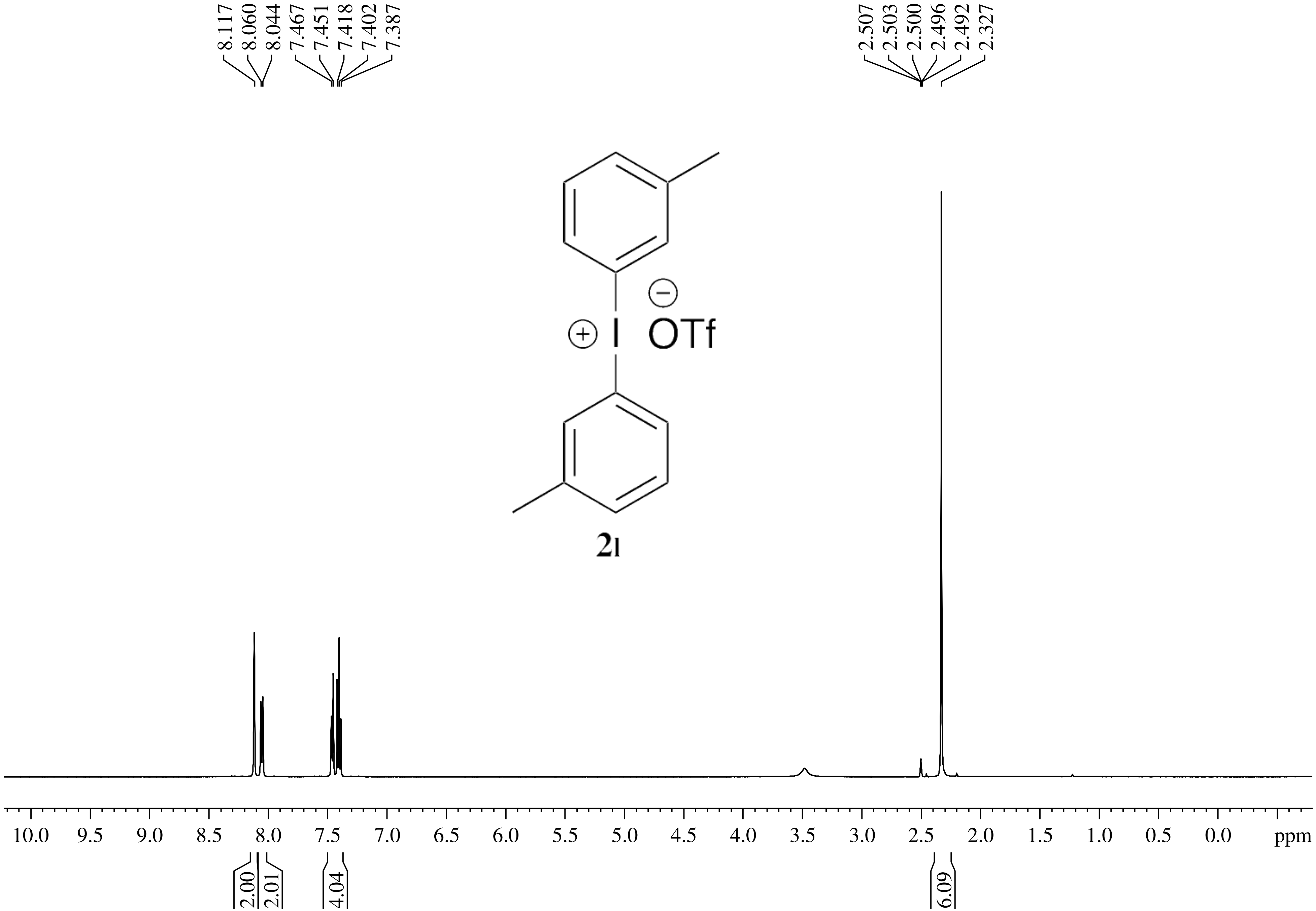


19F NMR, (CD3)2SO, 376 MHz

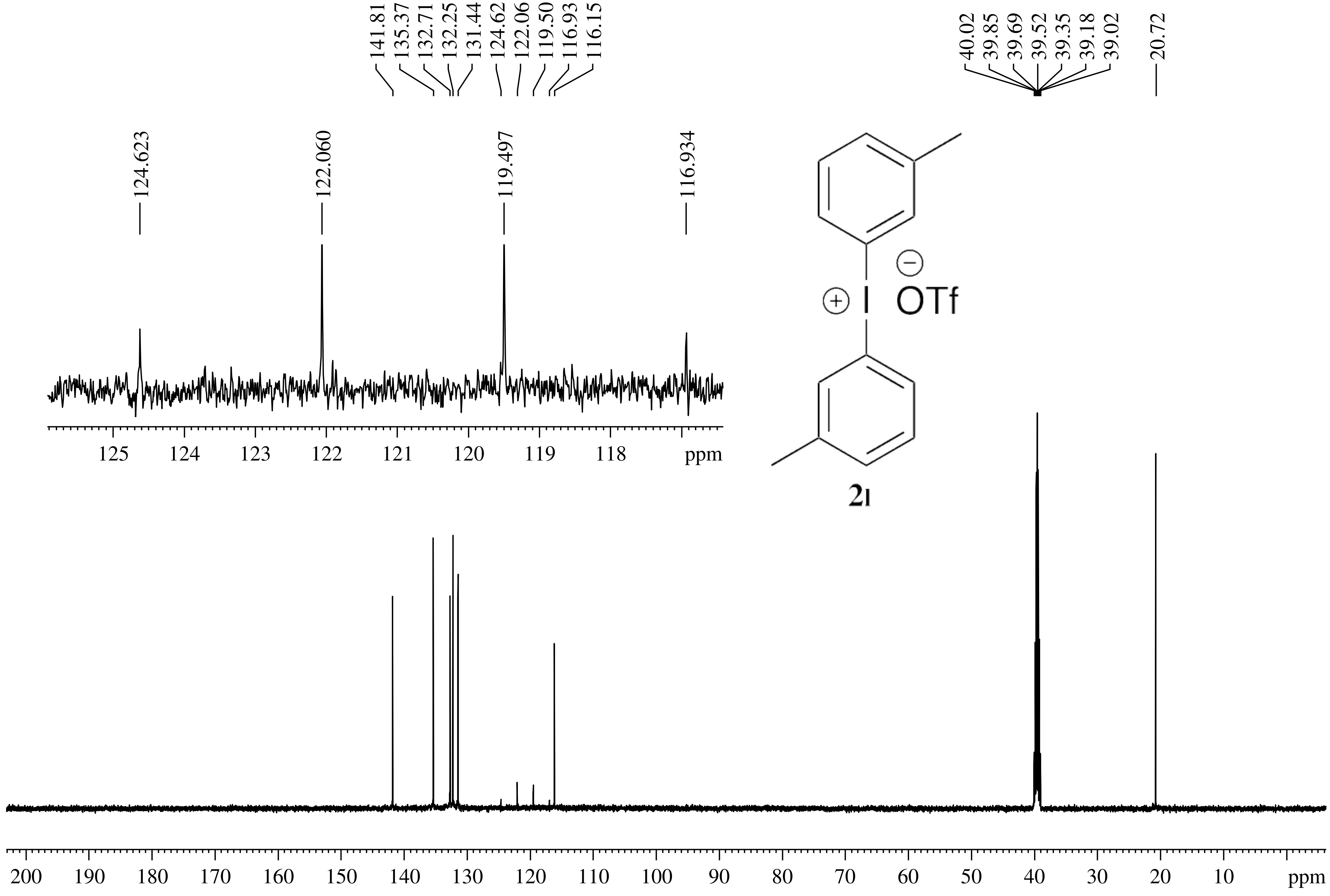


2k

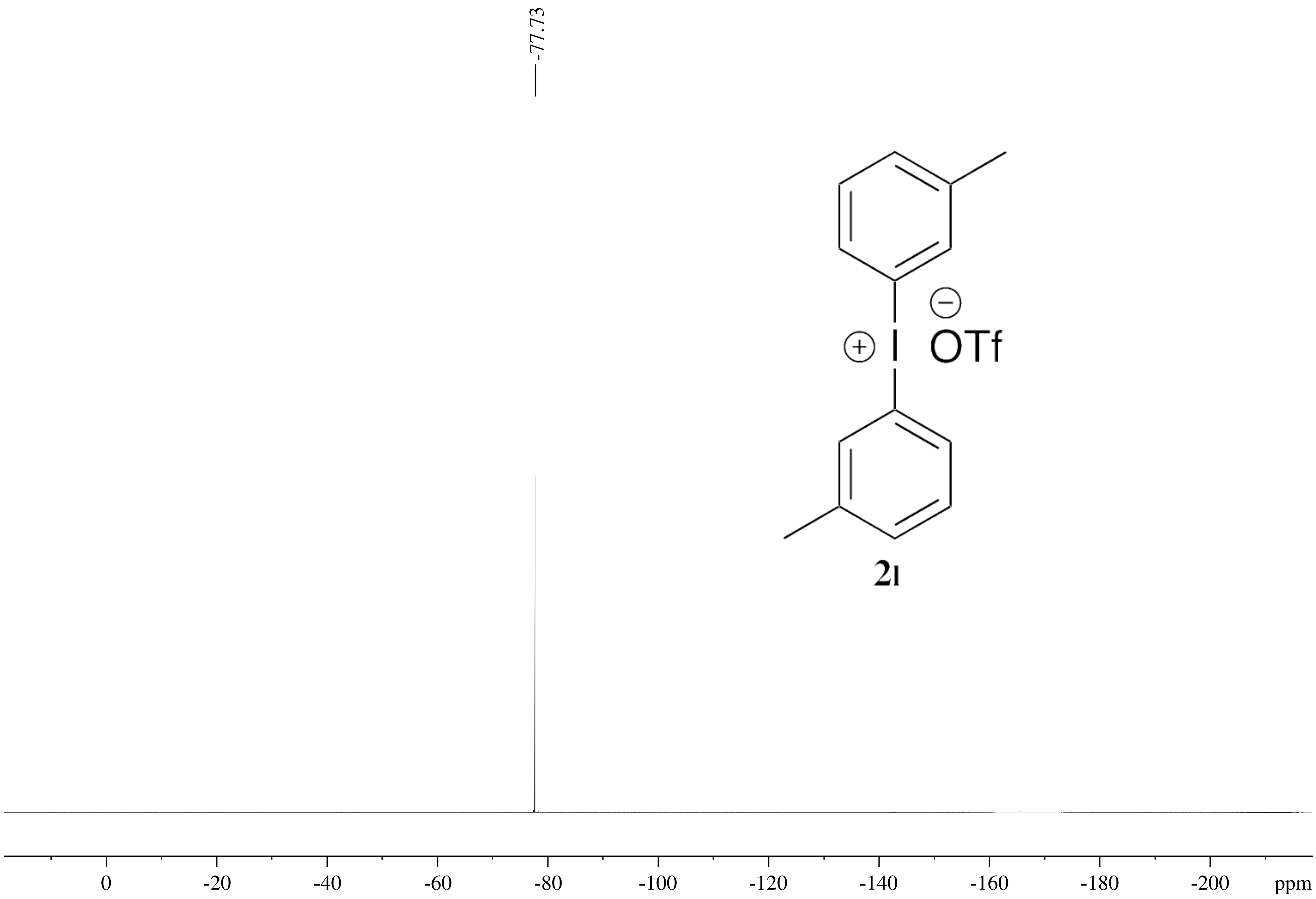
1H NMR, (CD3)2SO, 500 MHz



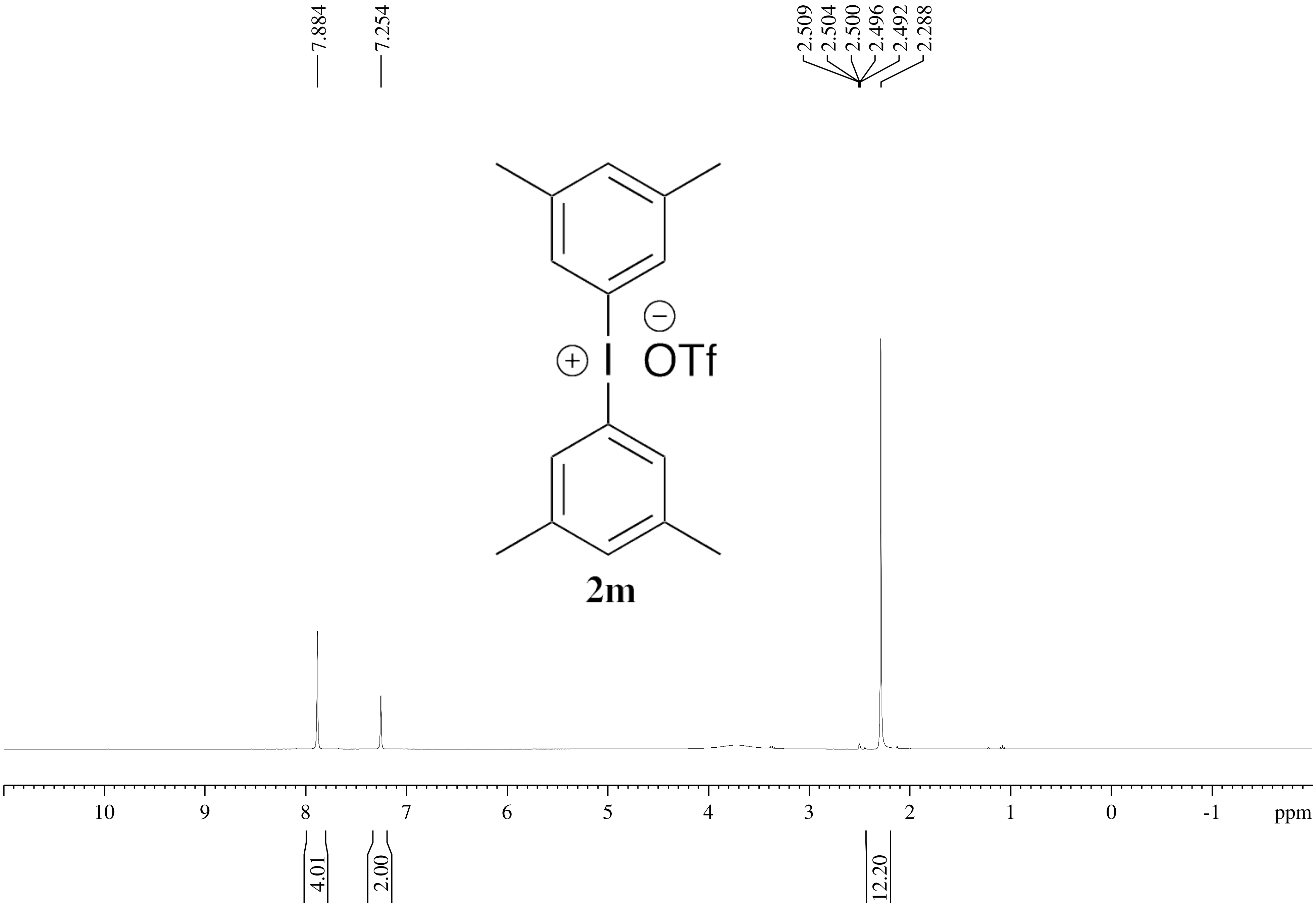
13C NMR, (CD3)2SO, 125 MHz



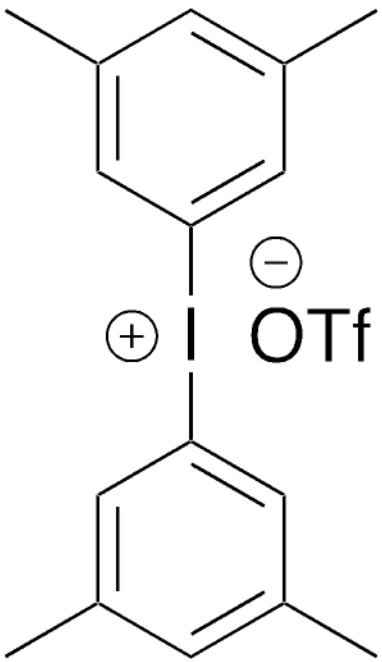
19F NMR, (CD3)2SO, 376 MHz



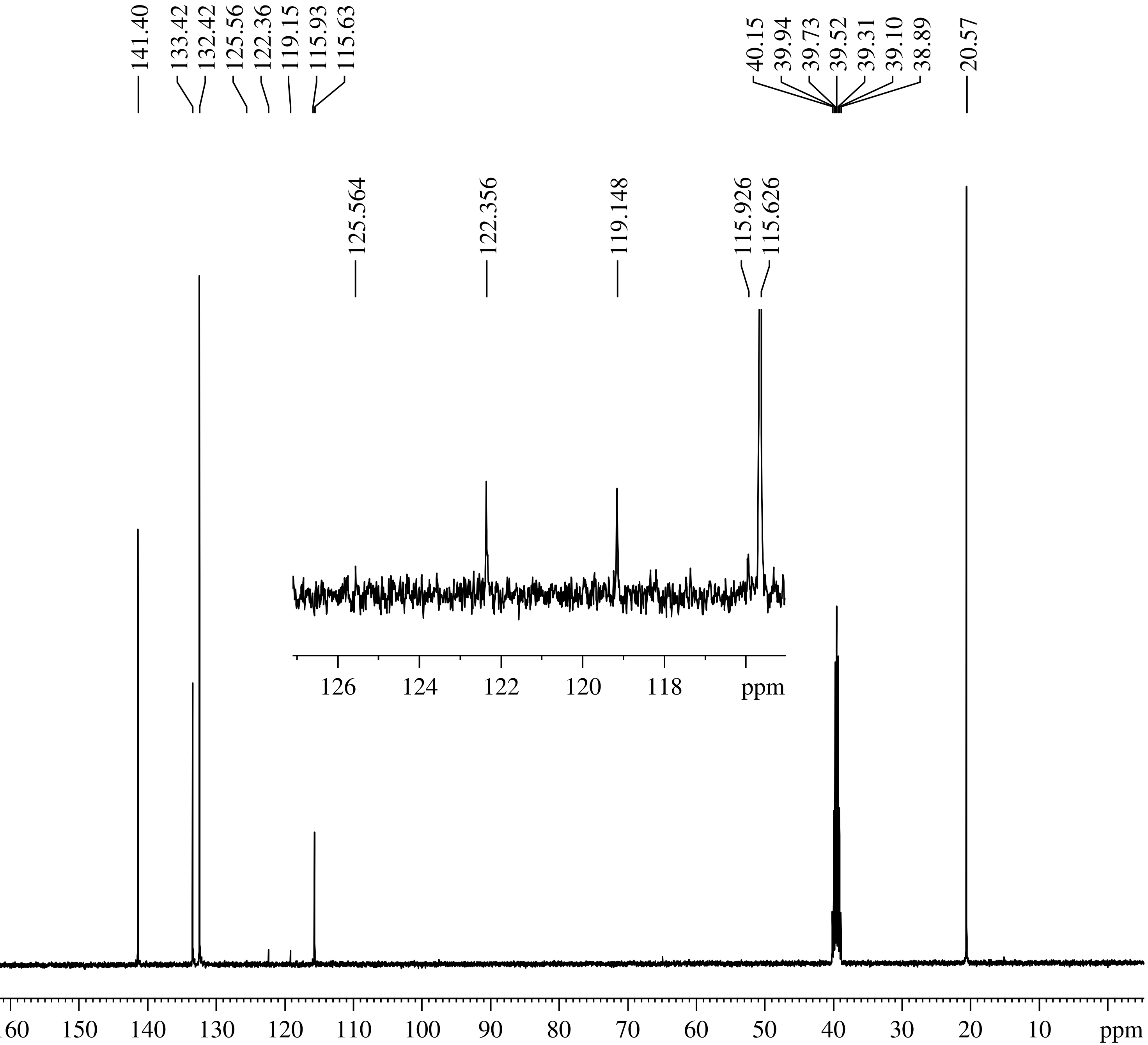
1H NMR, (CD3)2SO, 400 MHz



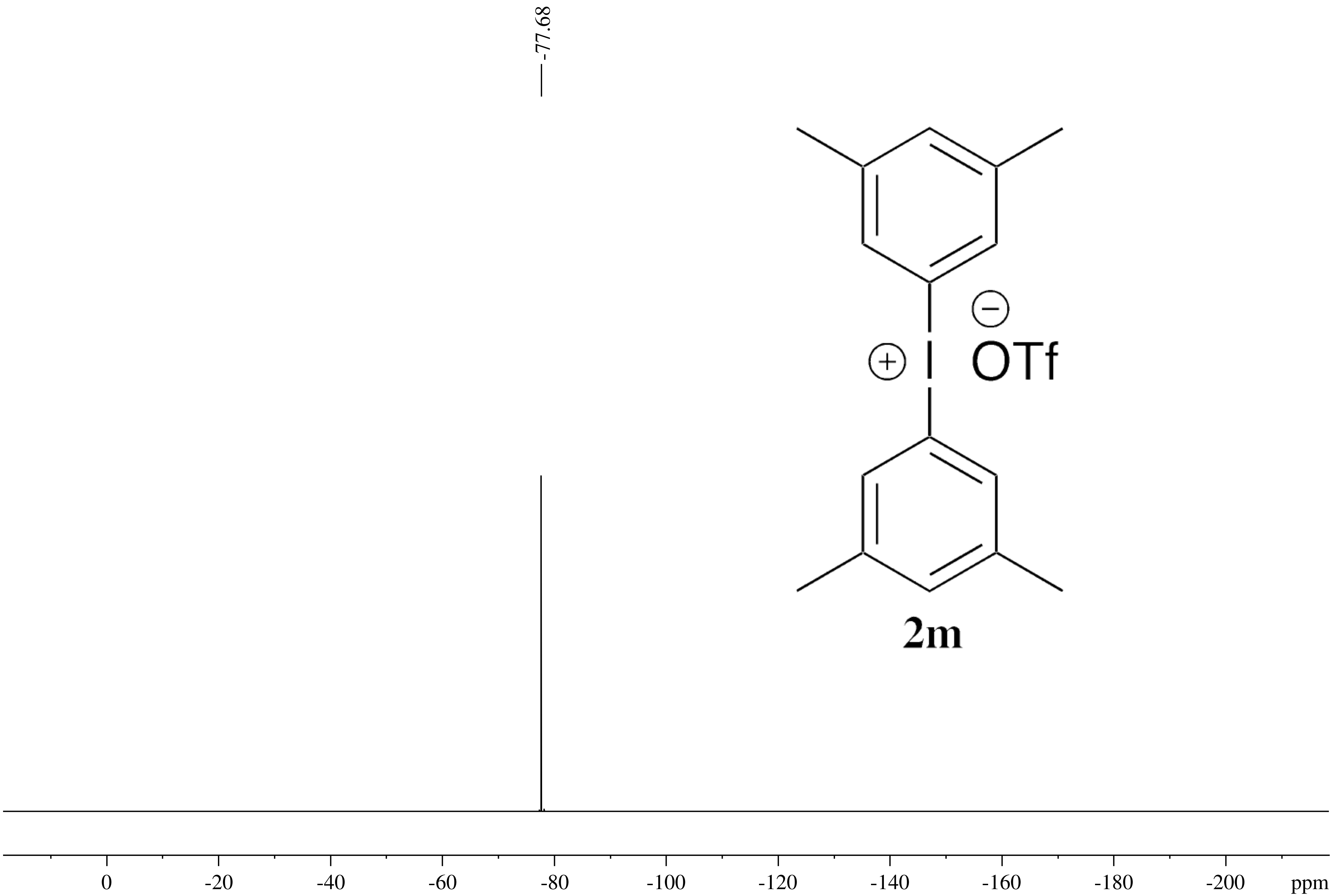
13C NMR, (CD3)2SO, 100 MHz



2m

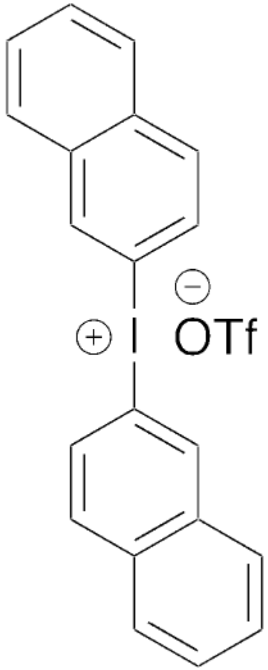


19F NMR, (CD3)2SO, 376 MHz

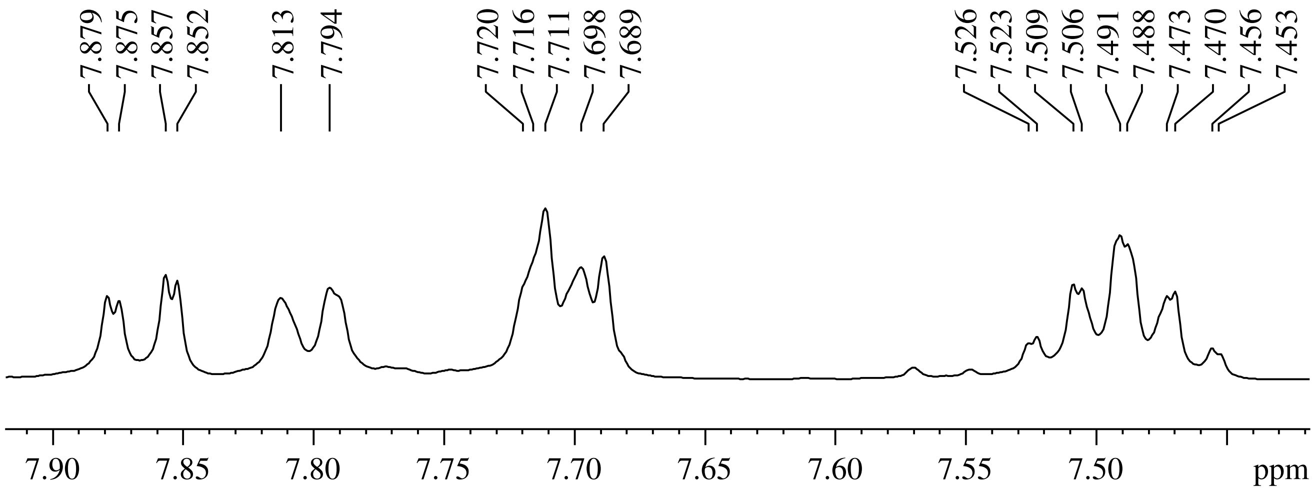


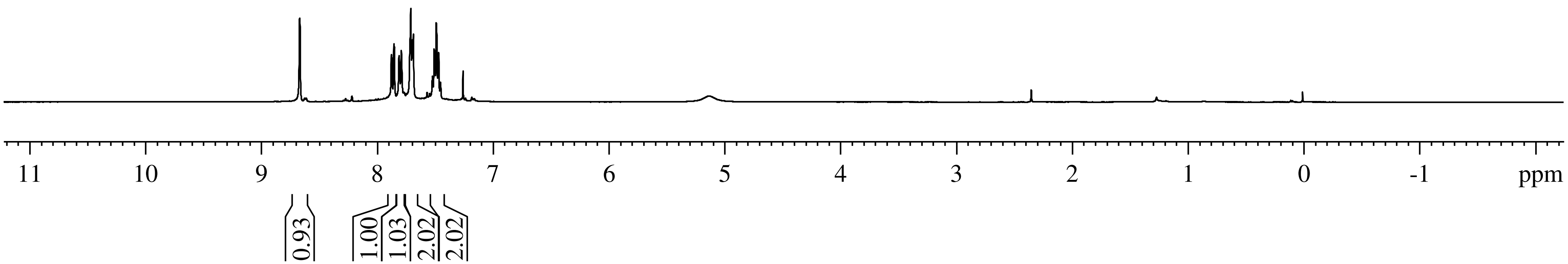
2m

1H NMR, CDCl3, 400 MHz

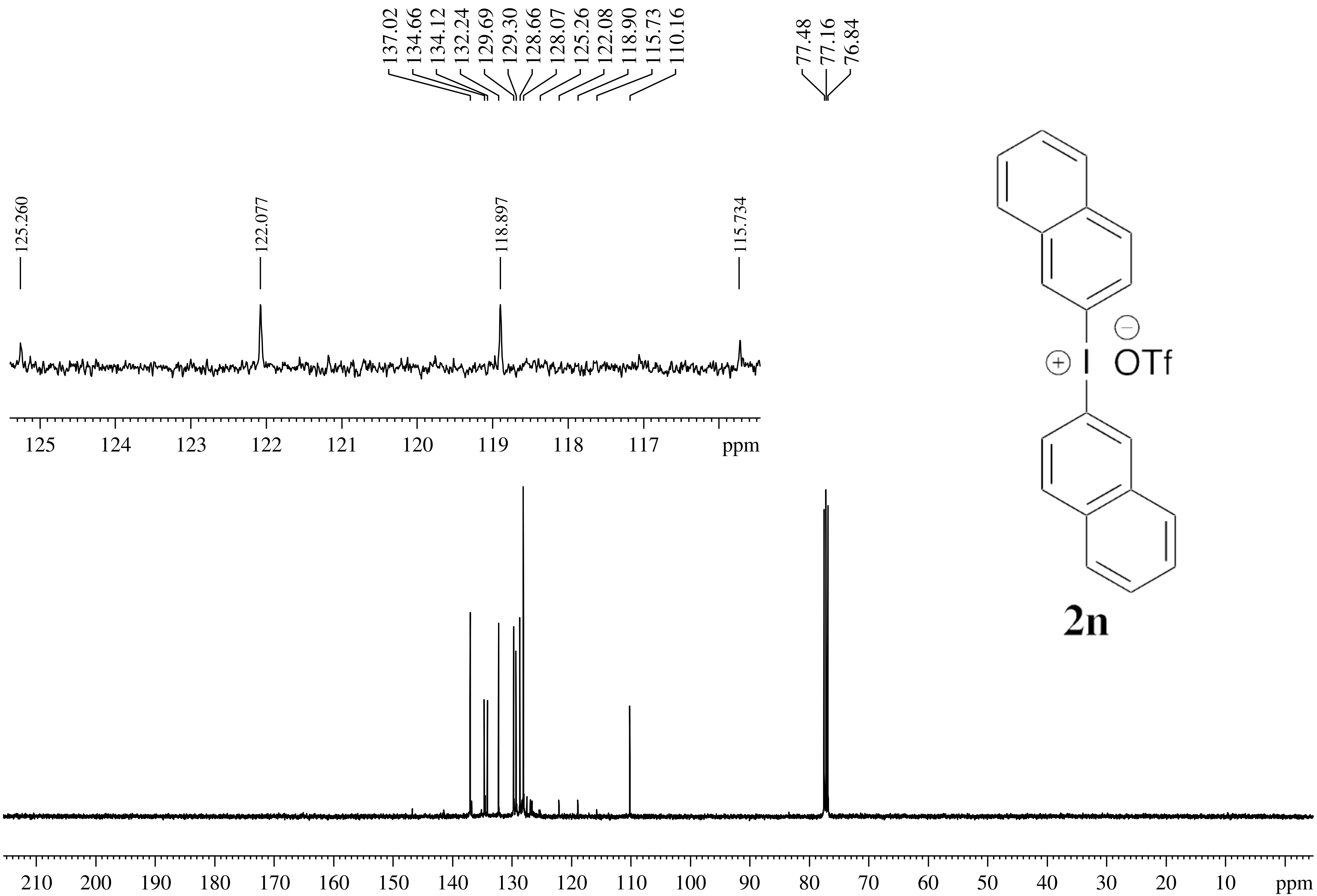


2n

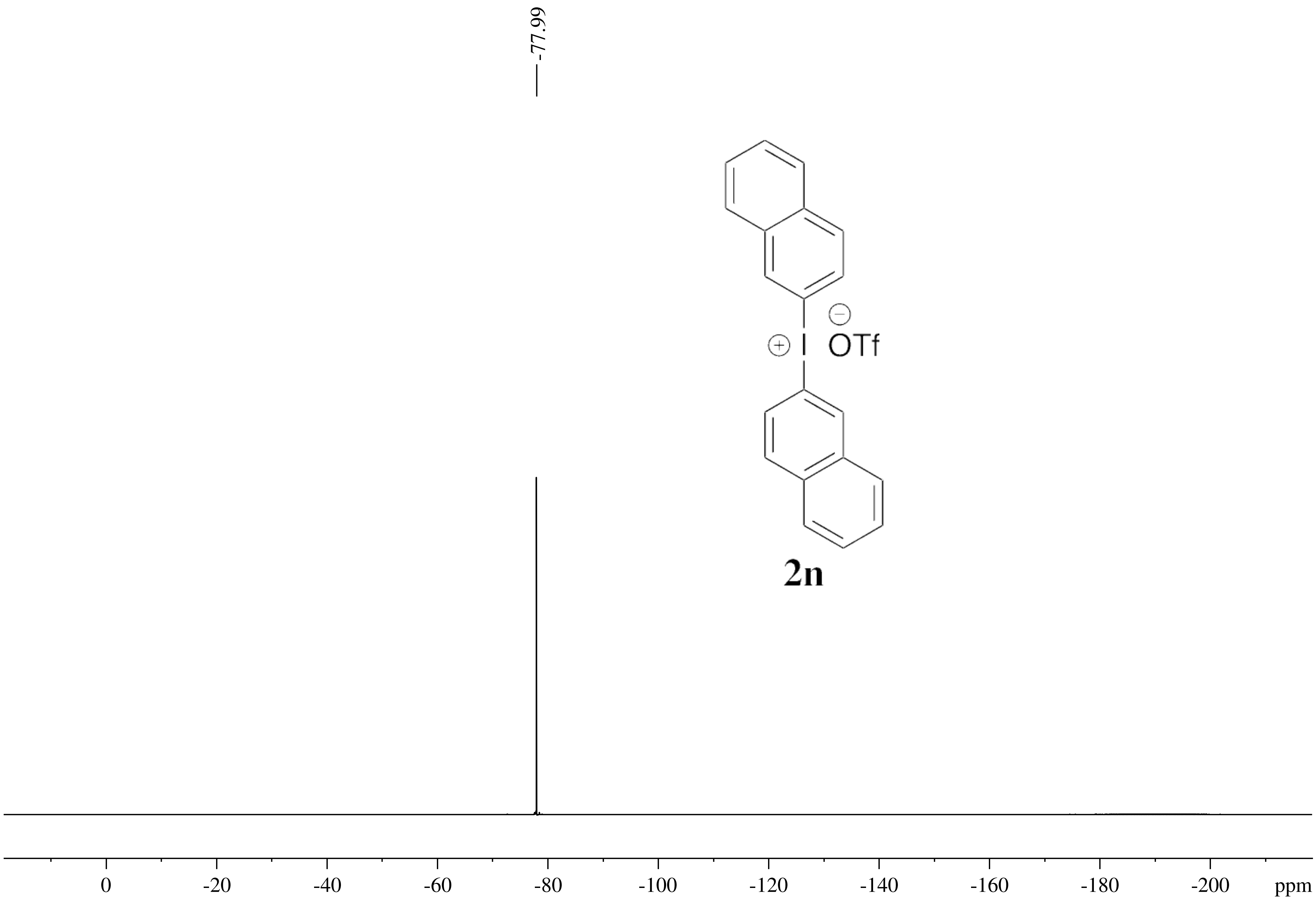




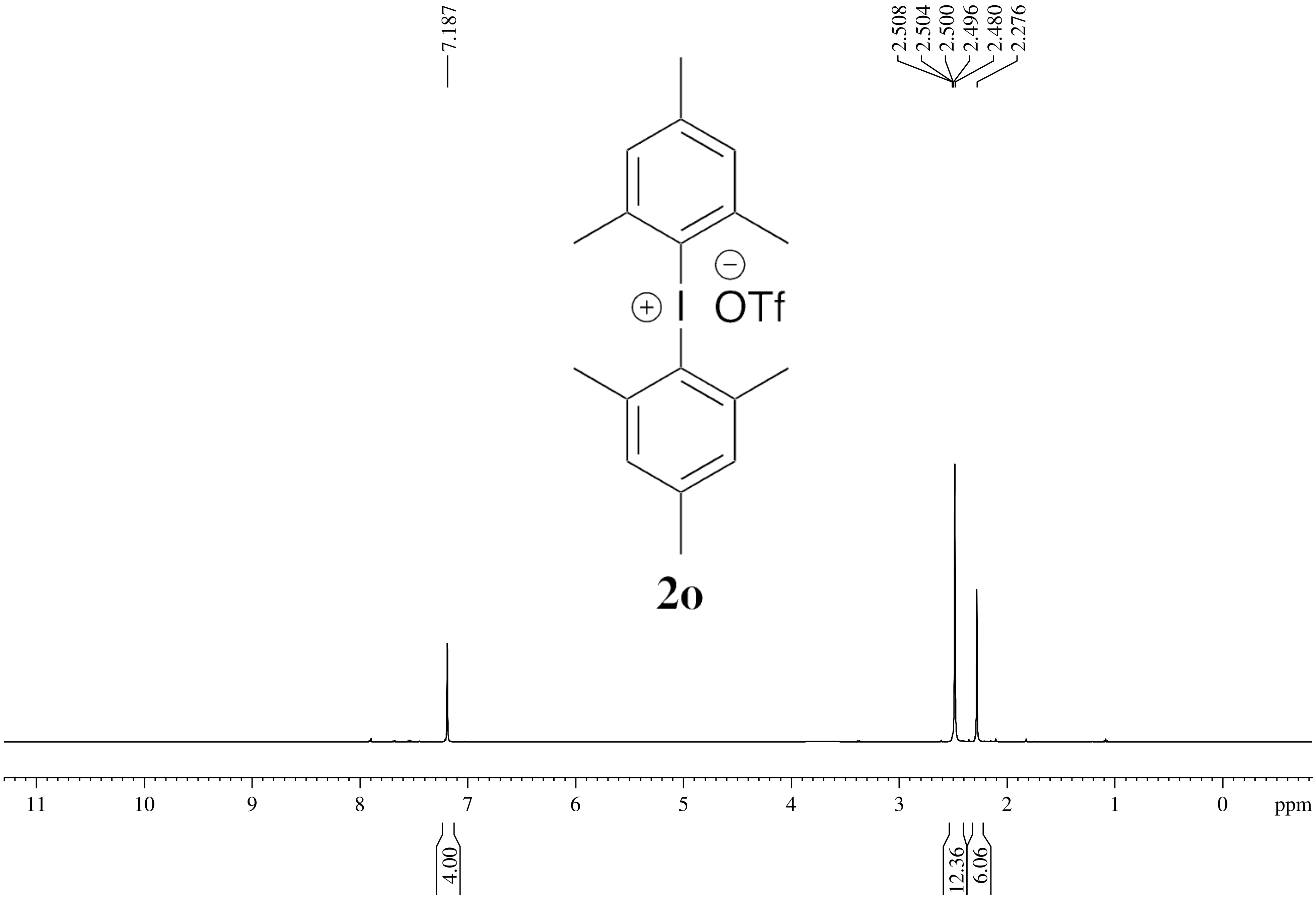
13C NMR, CDCl3, 100 MHz



19F NMR, CDCl3, 376 MHz

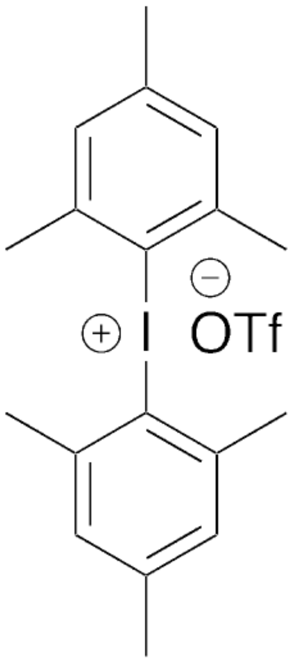


1H NMR, (CD3)2SO, 500 MHz

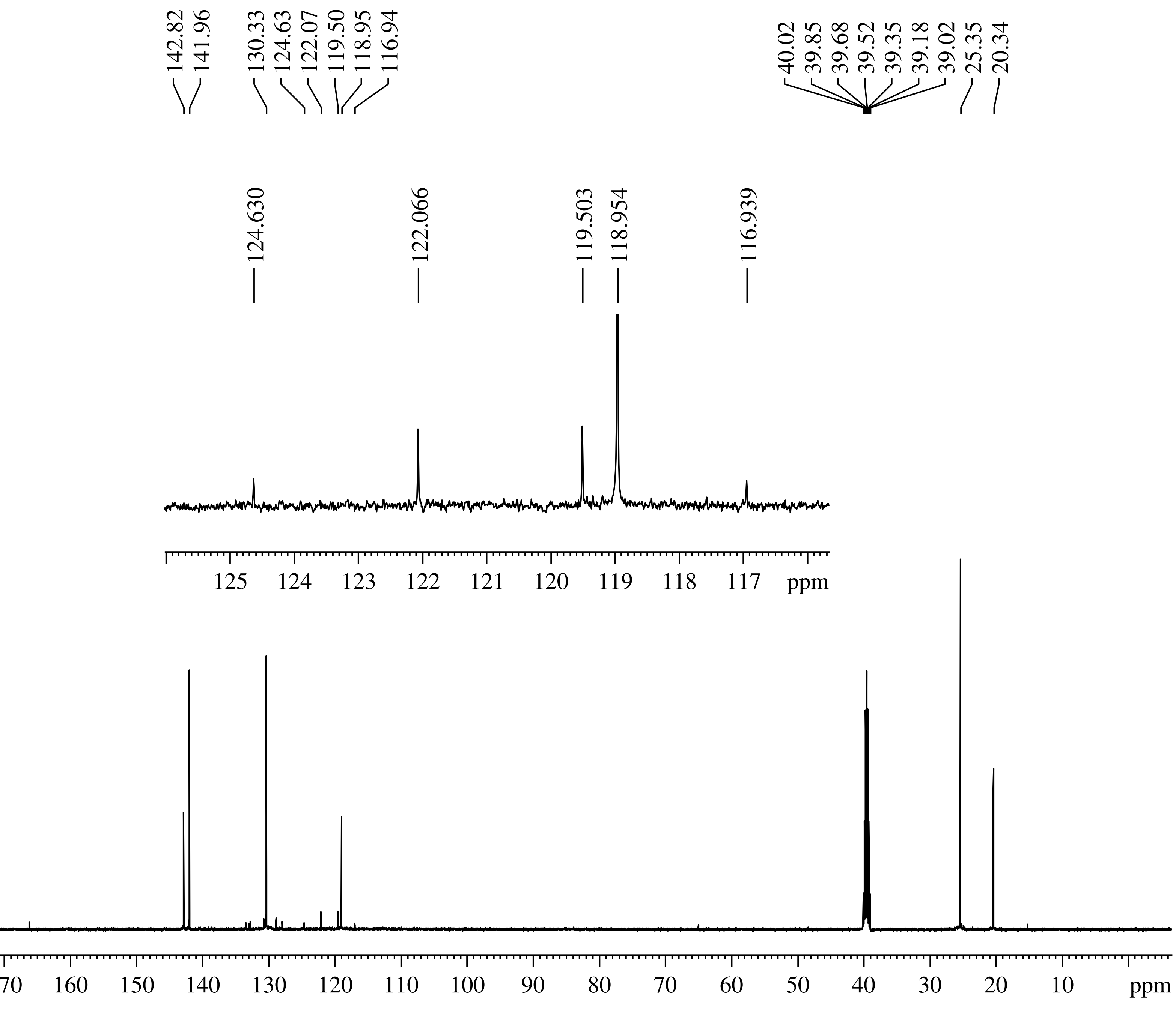


2o

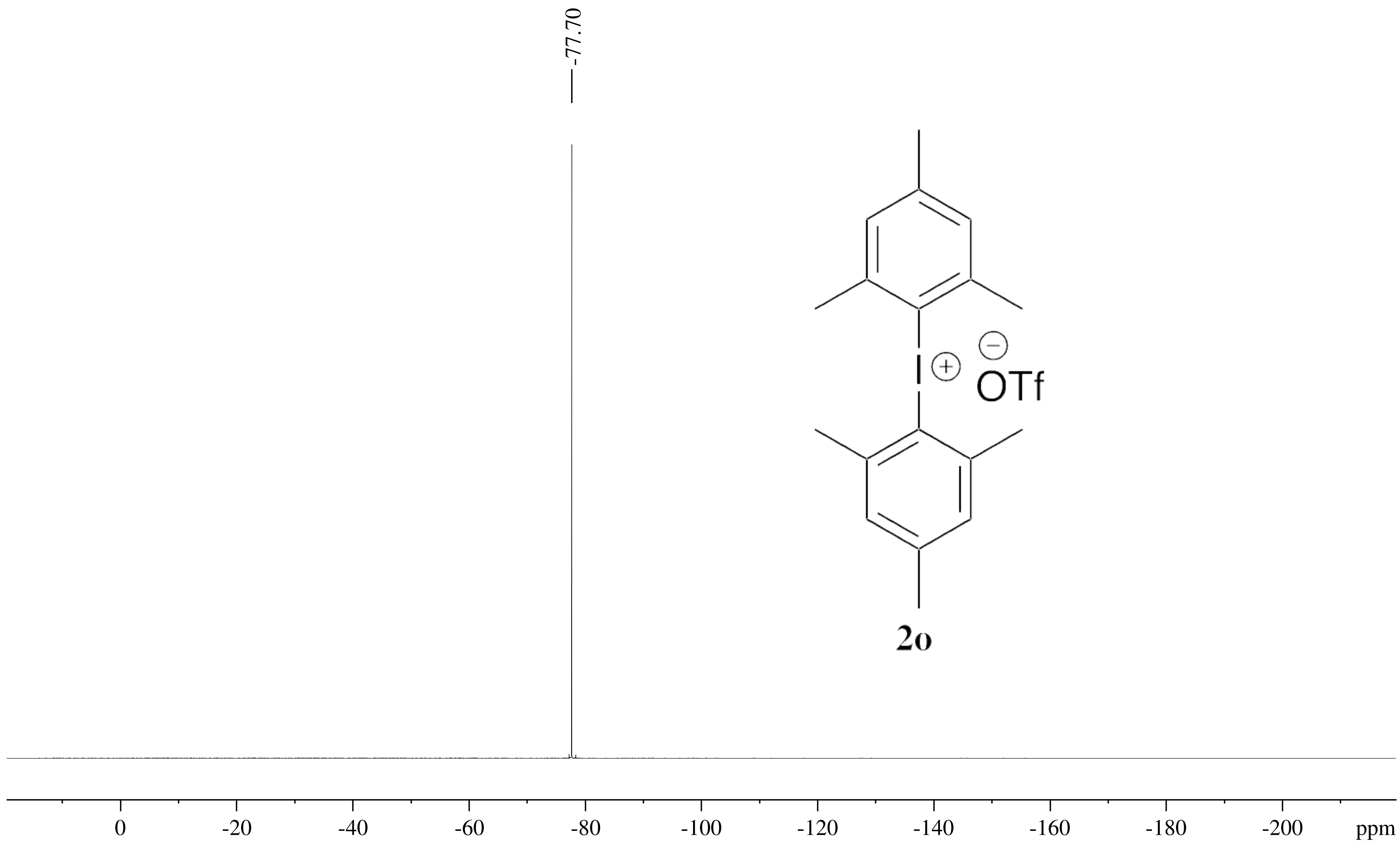
13C NMR, (CD3)2SO, 125 MHz



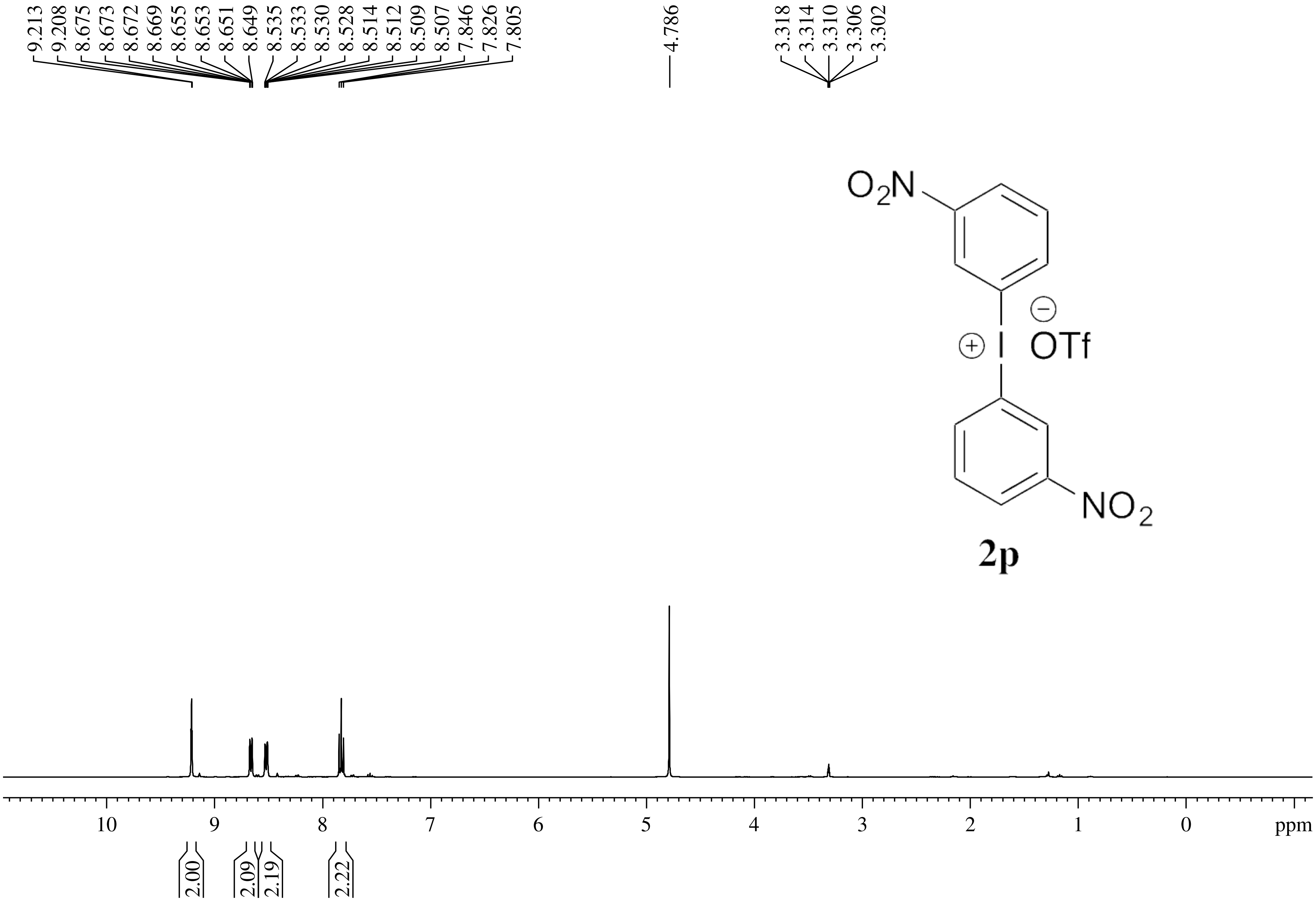
2o



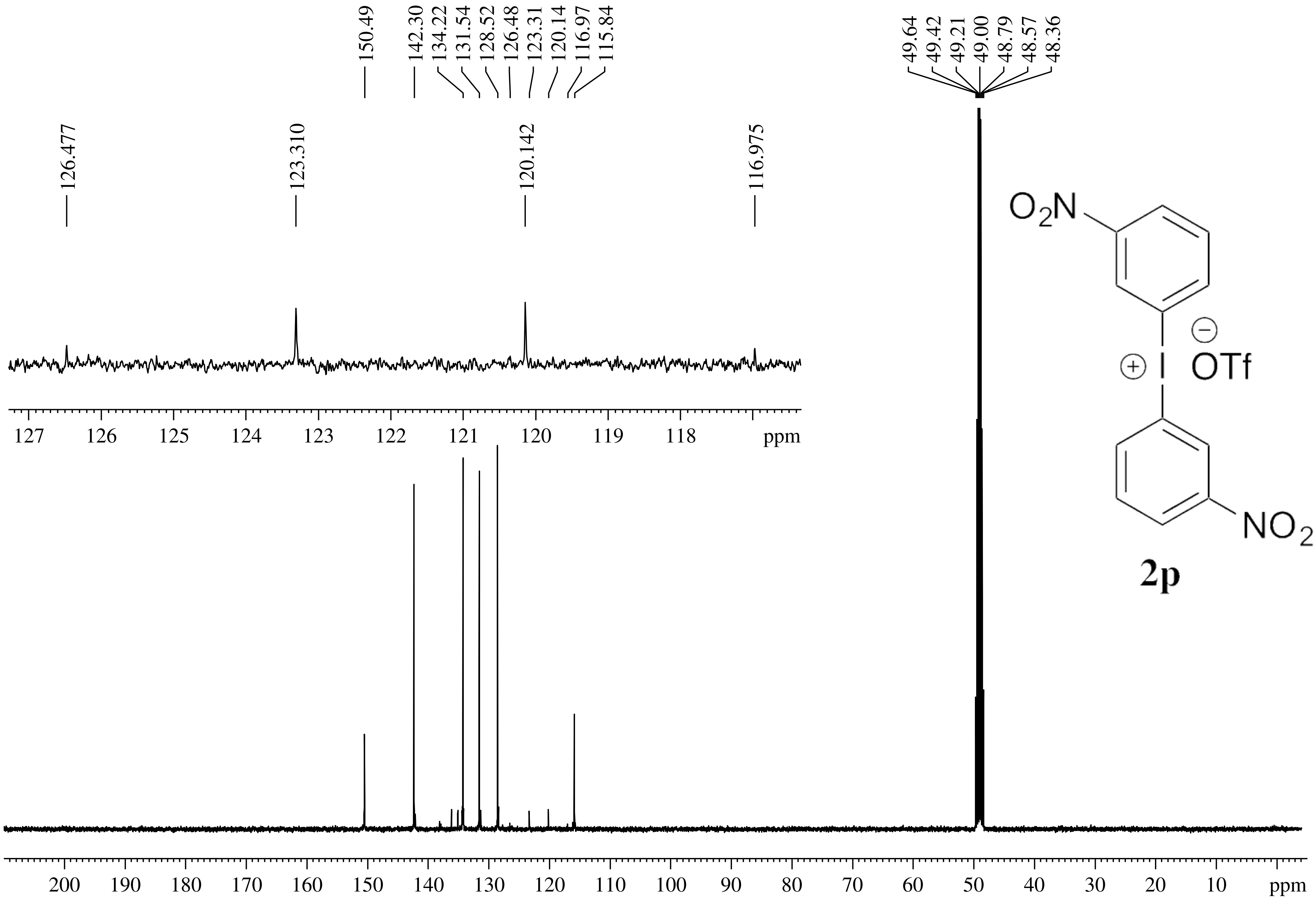
^{19}F NMR, $(CD_3)_2SO$, 282 MHz



1H NMR, CD3OD, 400 MHz

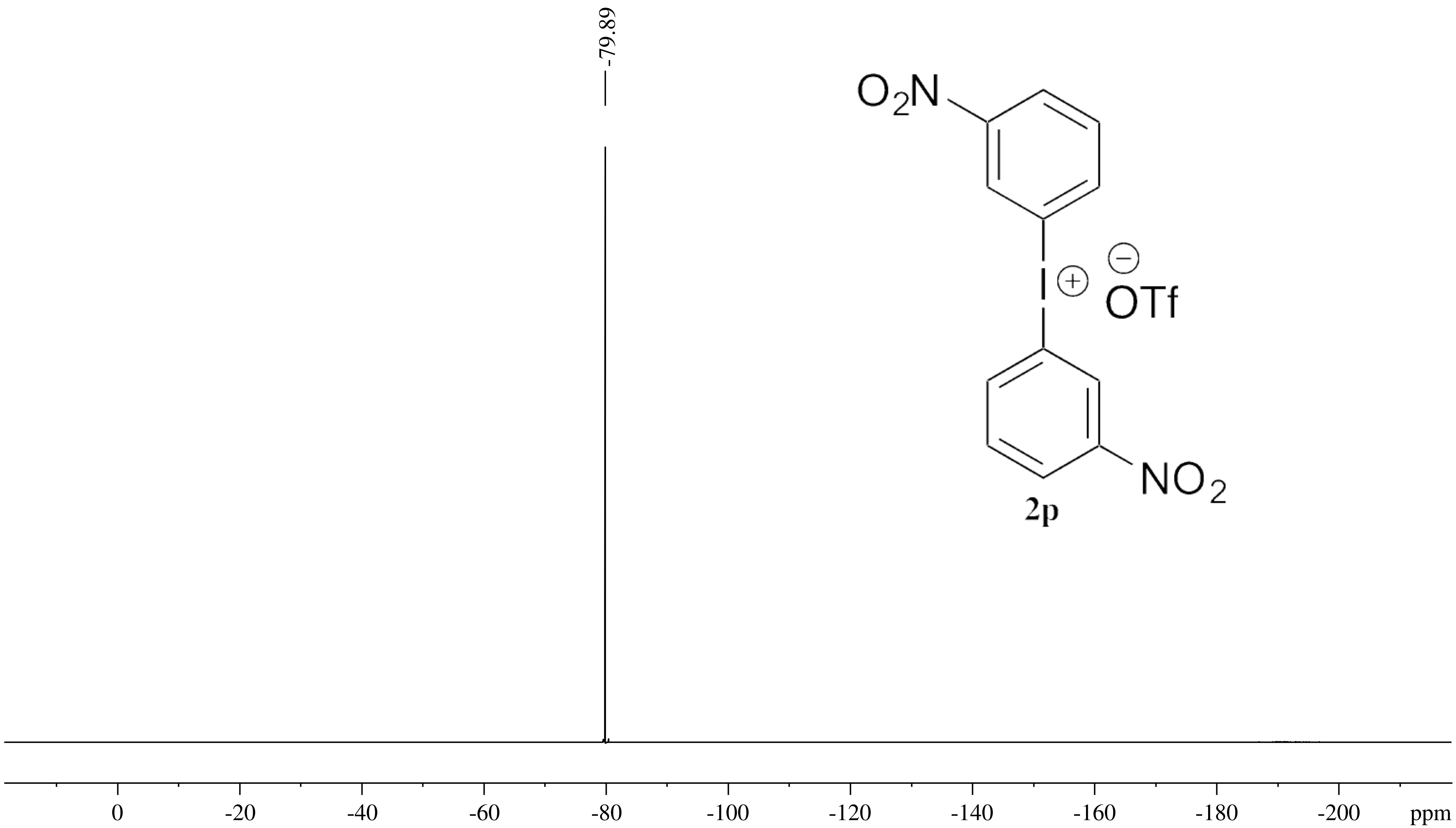


13C NMR, CD3OD, 100 MHz

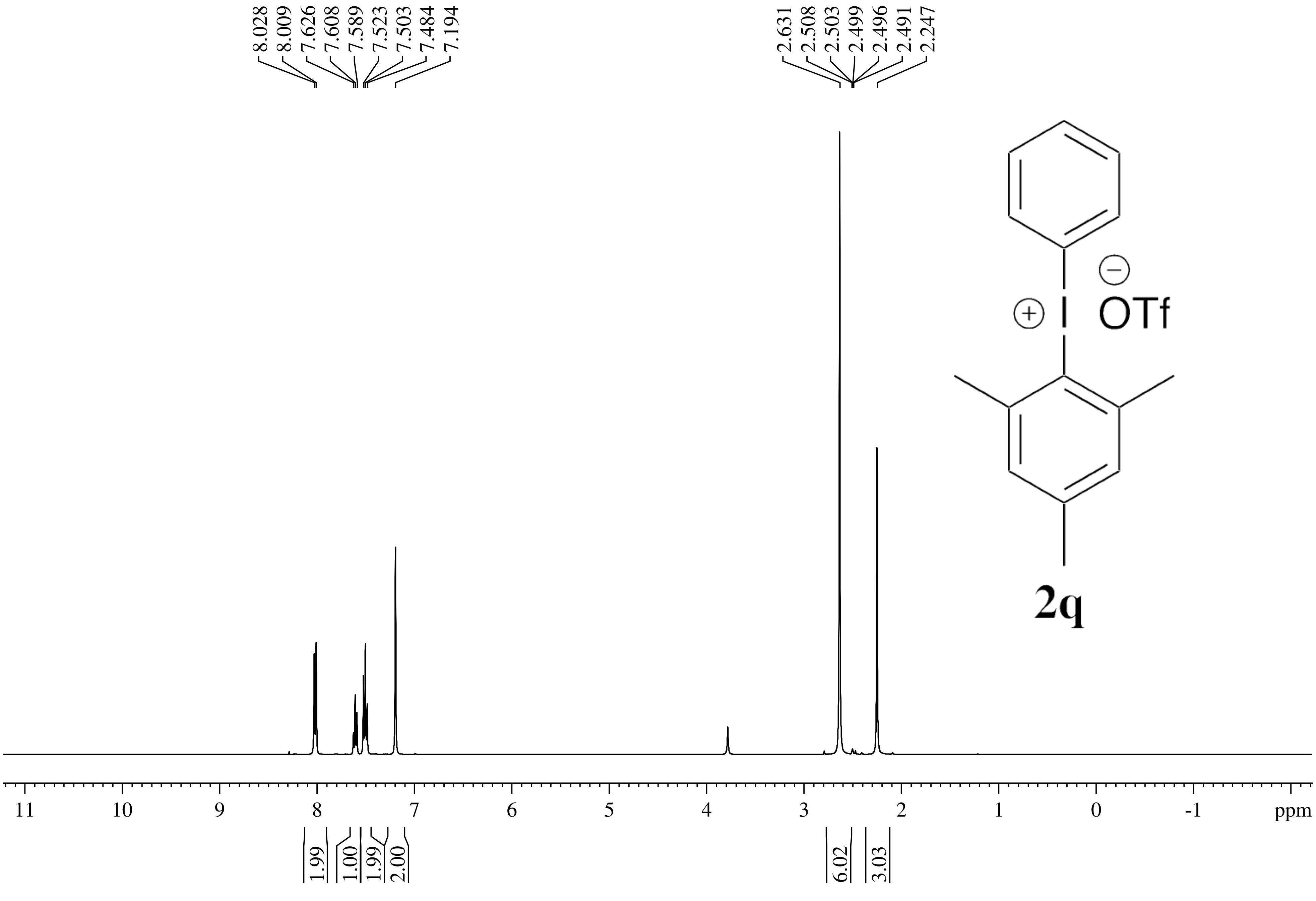


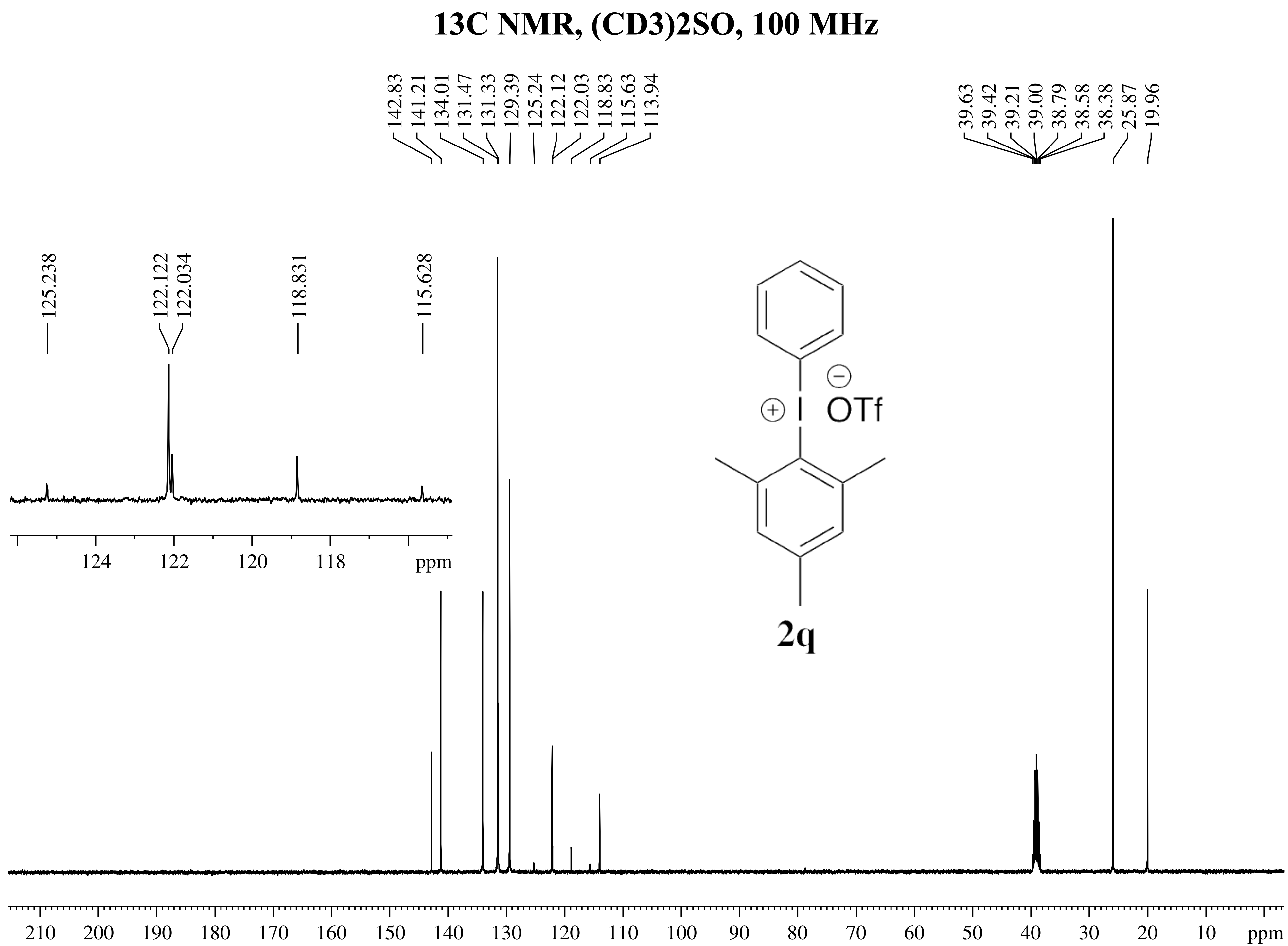
2p

^{19}F NMR, $(CD_3)_2SO$, 376 MHz



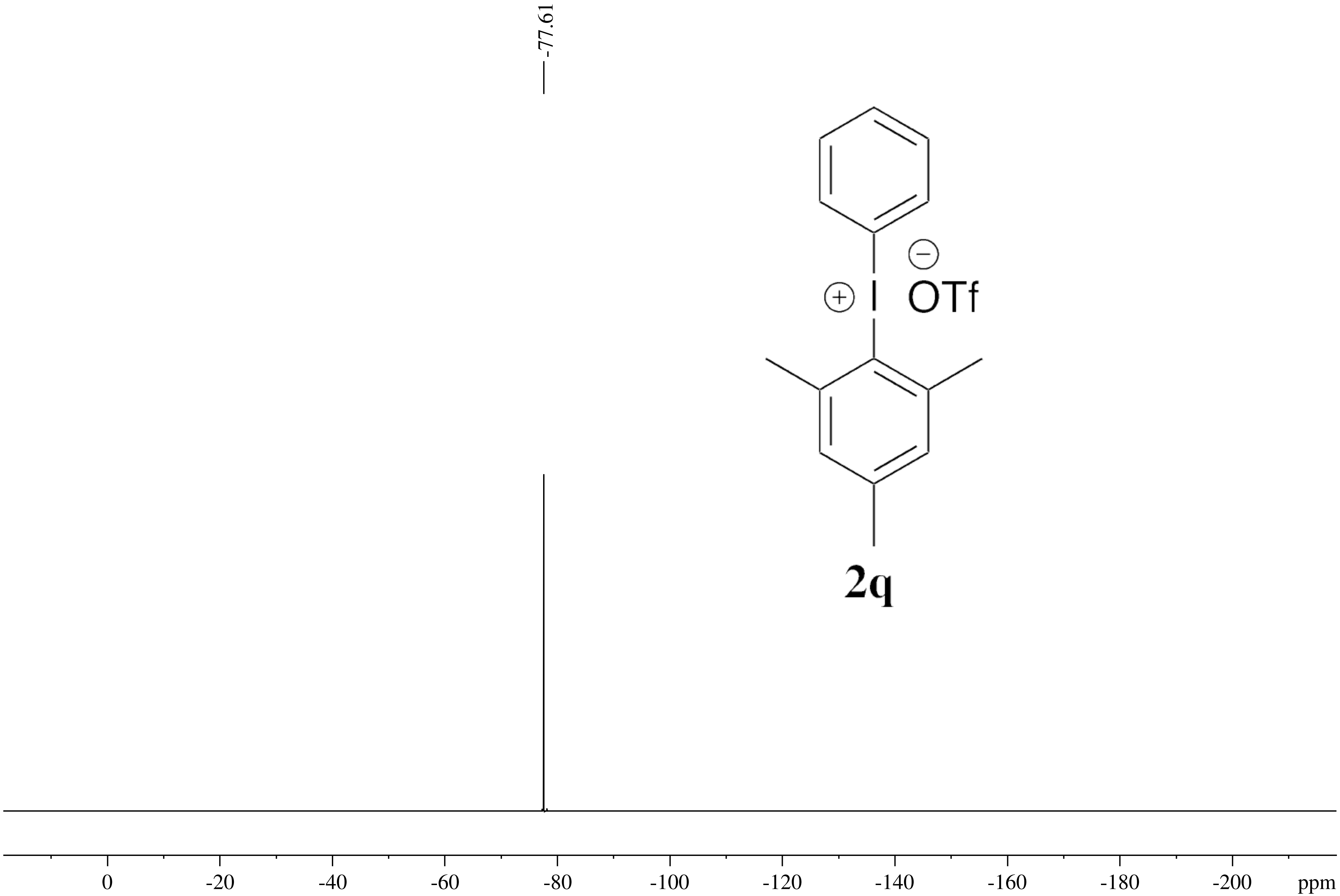
1H NMR, (CD3)2SO, 400 MHz



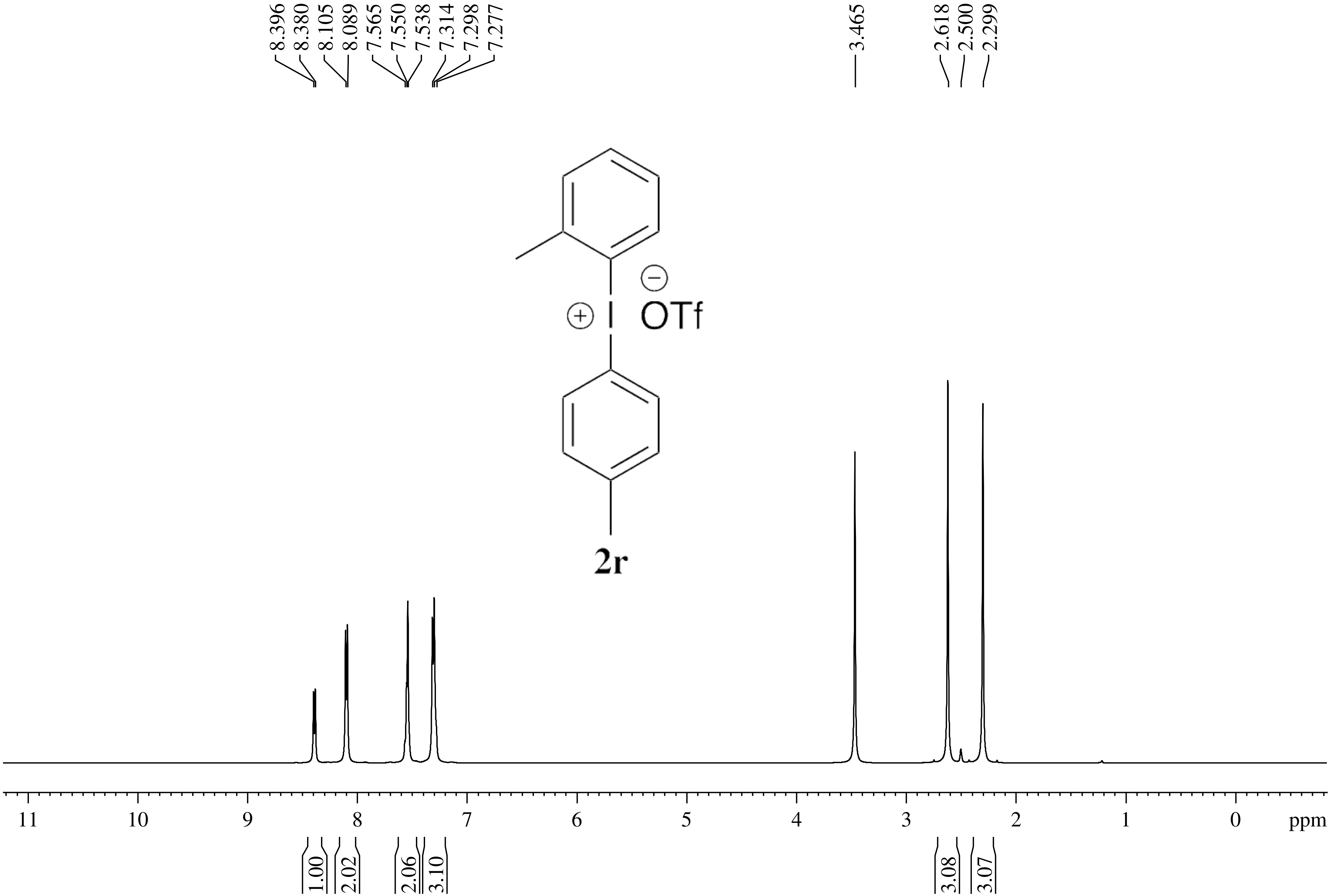


13C NMR, (CD3)2SO, 100 MHz
142.83
141.21
134.01
131.47
131.33
129.39
125.24
122.12
122.03
118.83
115.63
113.94
39.63
39.42
39.21
39.00
38.79
38.58
38.38
25.87
19.96
125.238
122.122
122.034
118.831
115.628
124
122
120
118
ppm
OTf
2q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

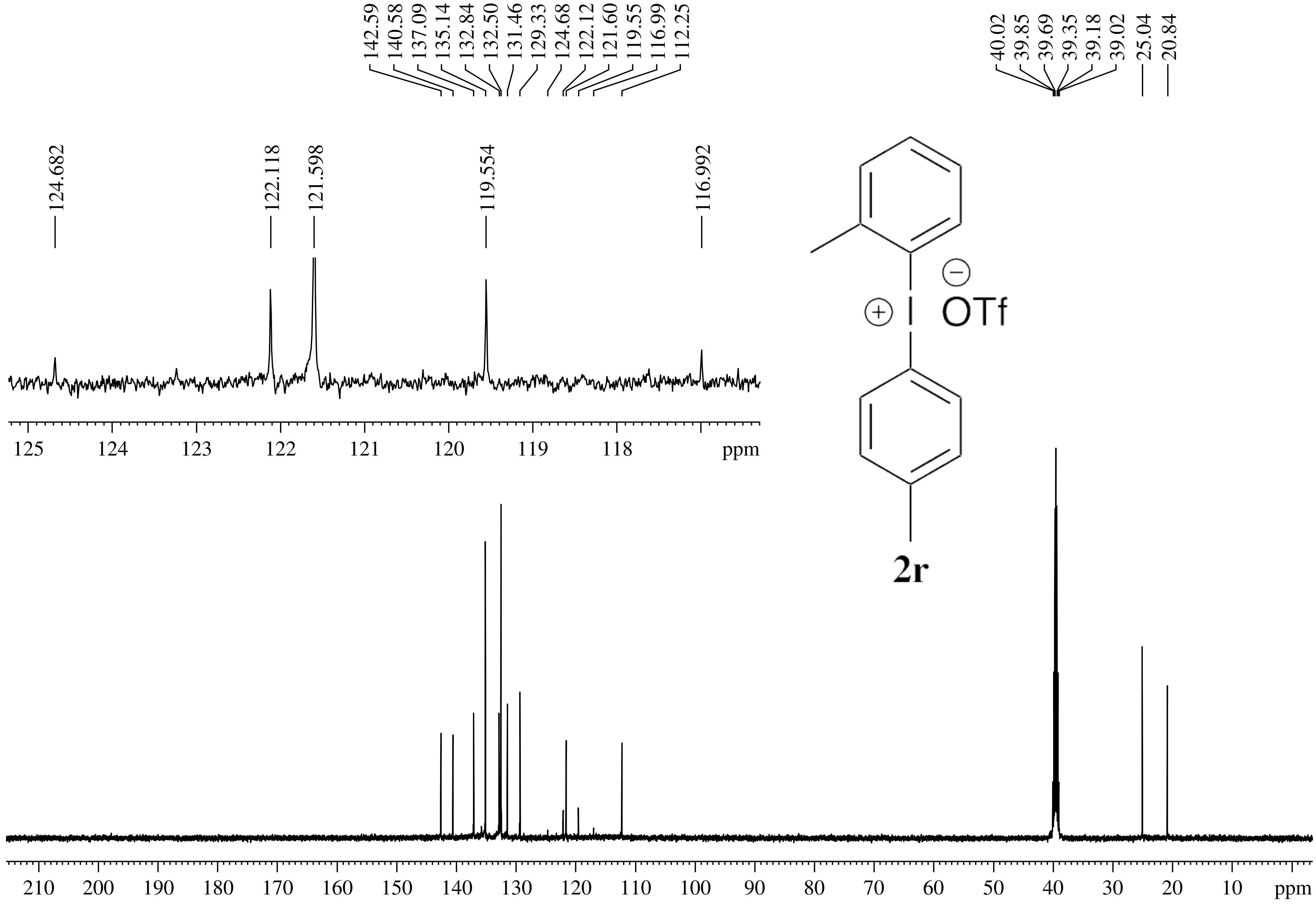
19F NMR, (CD3)2SO, 376 MHz



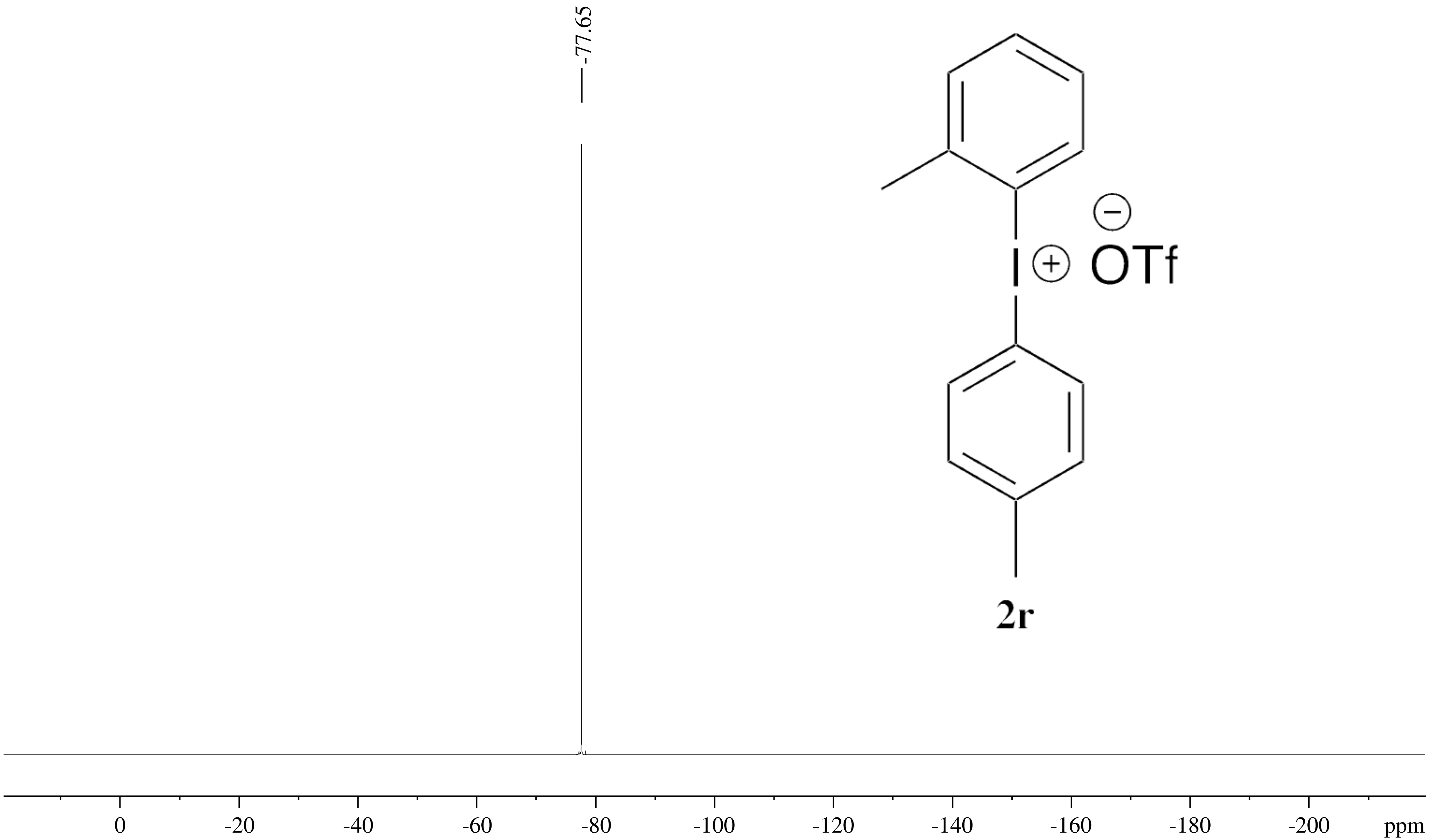
1H NMR, (CD3)2SO, 500 MHz



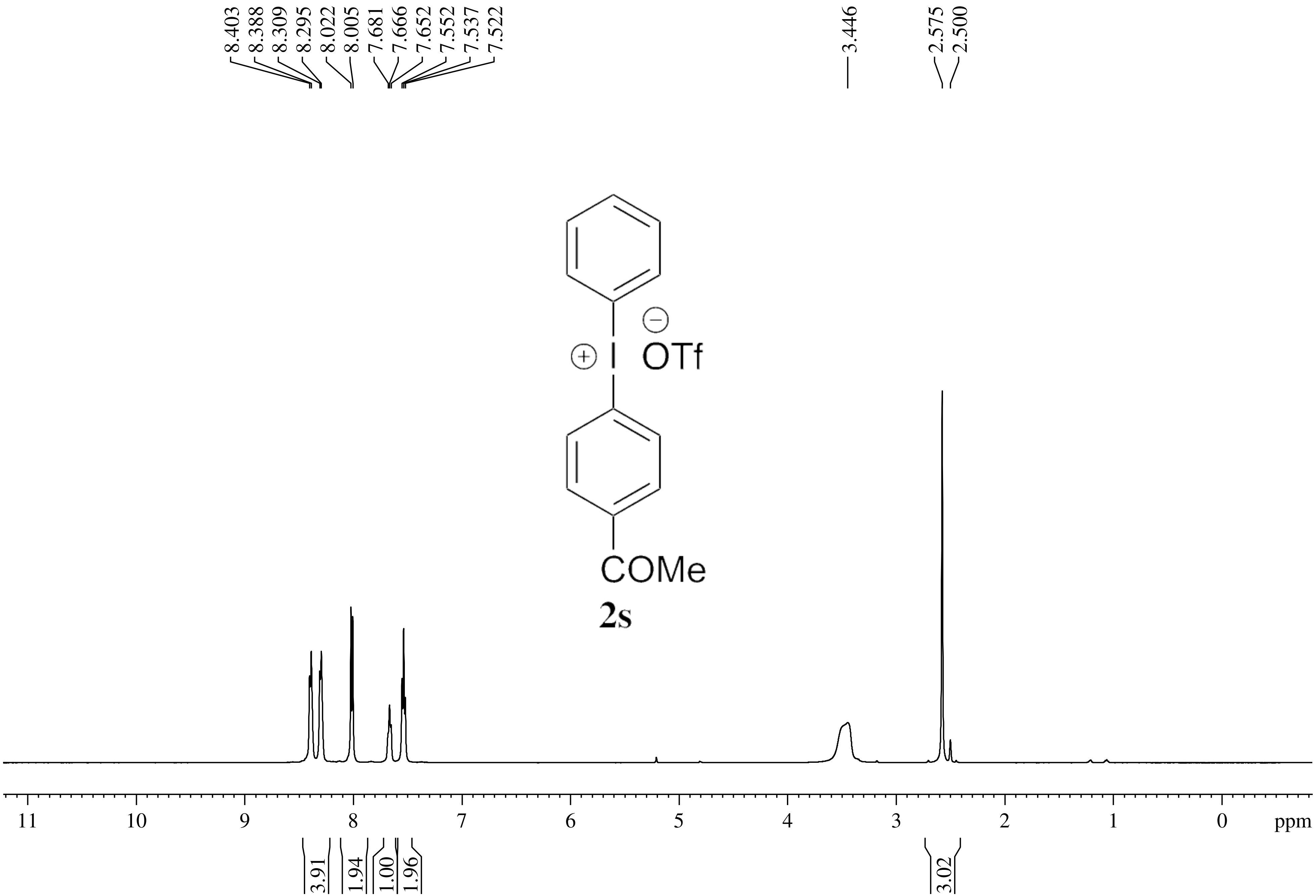
13C NMR, (CD3)2SO, 125 MHz



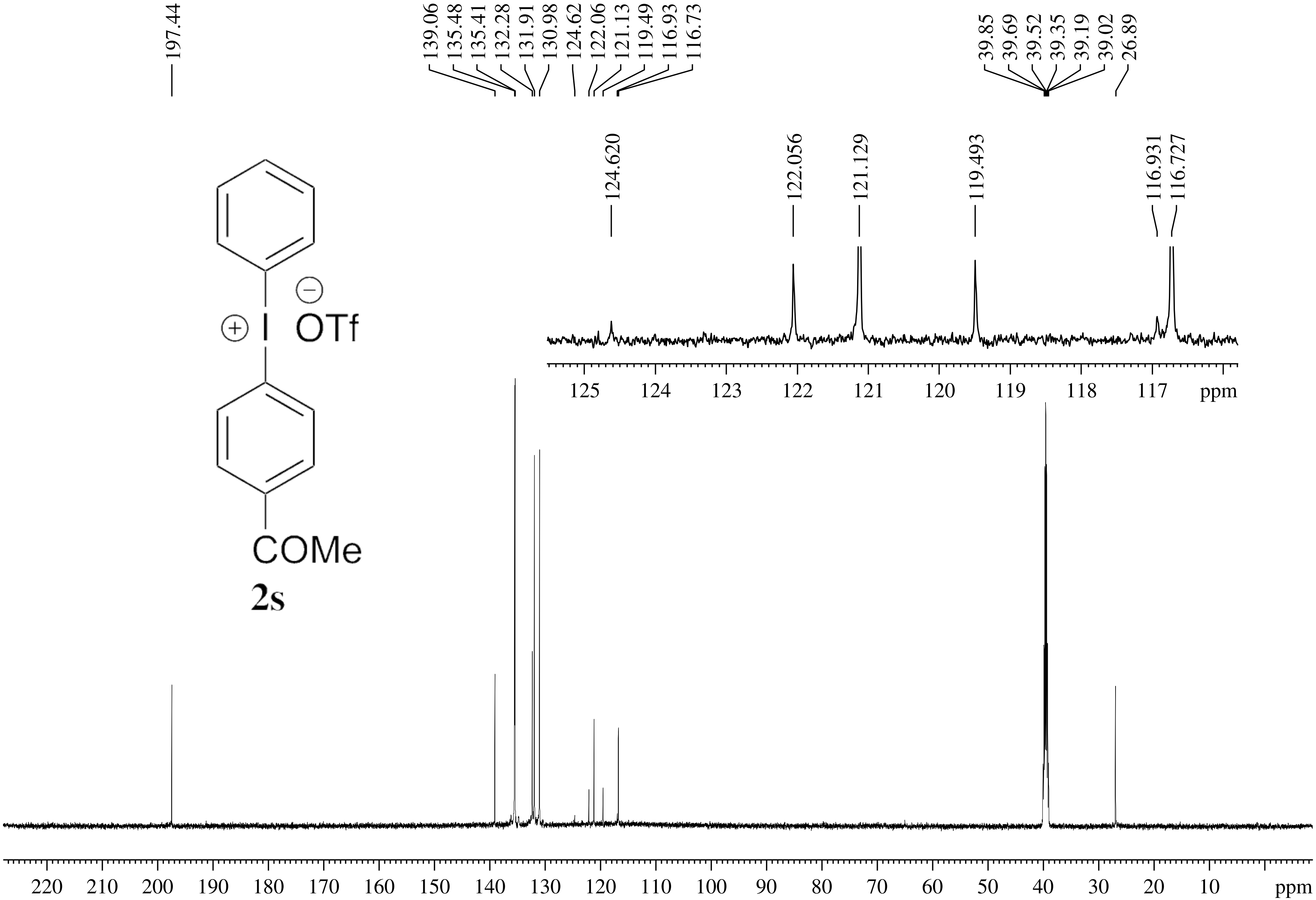
^{19}F NMR, $(CD_3)_2SO$, 282 MHz



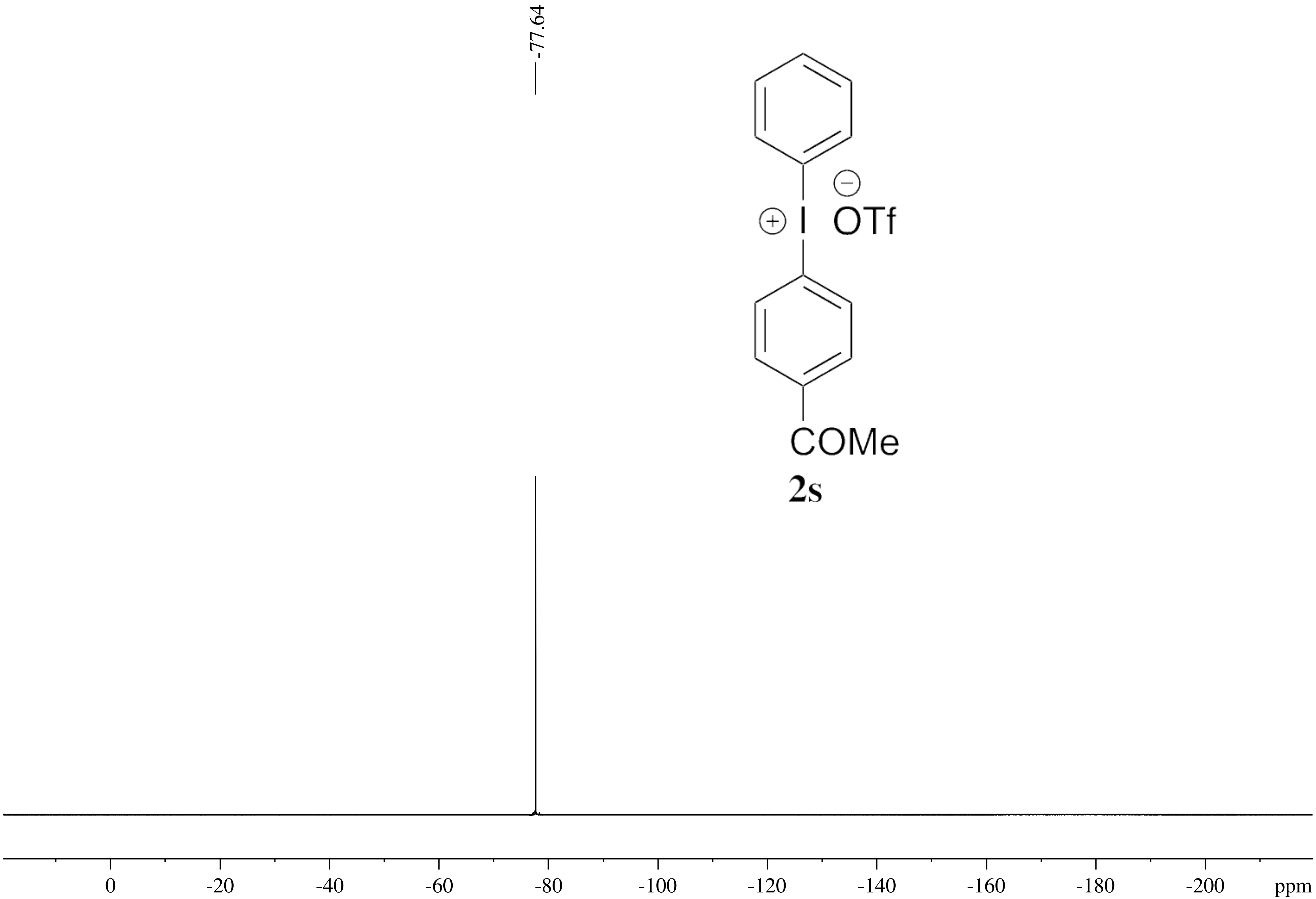
1H NMR, (CD3)2SO, 500 MHz



1H NMR, (CD3)2SO, 125 MHz

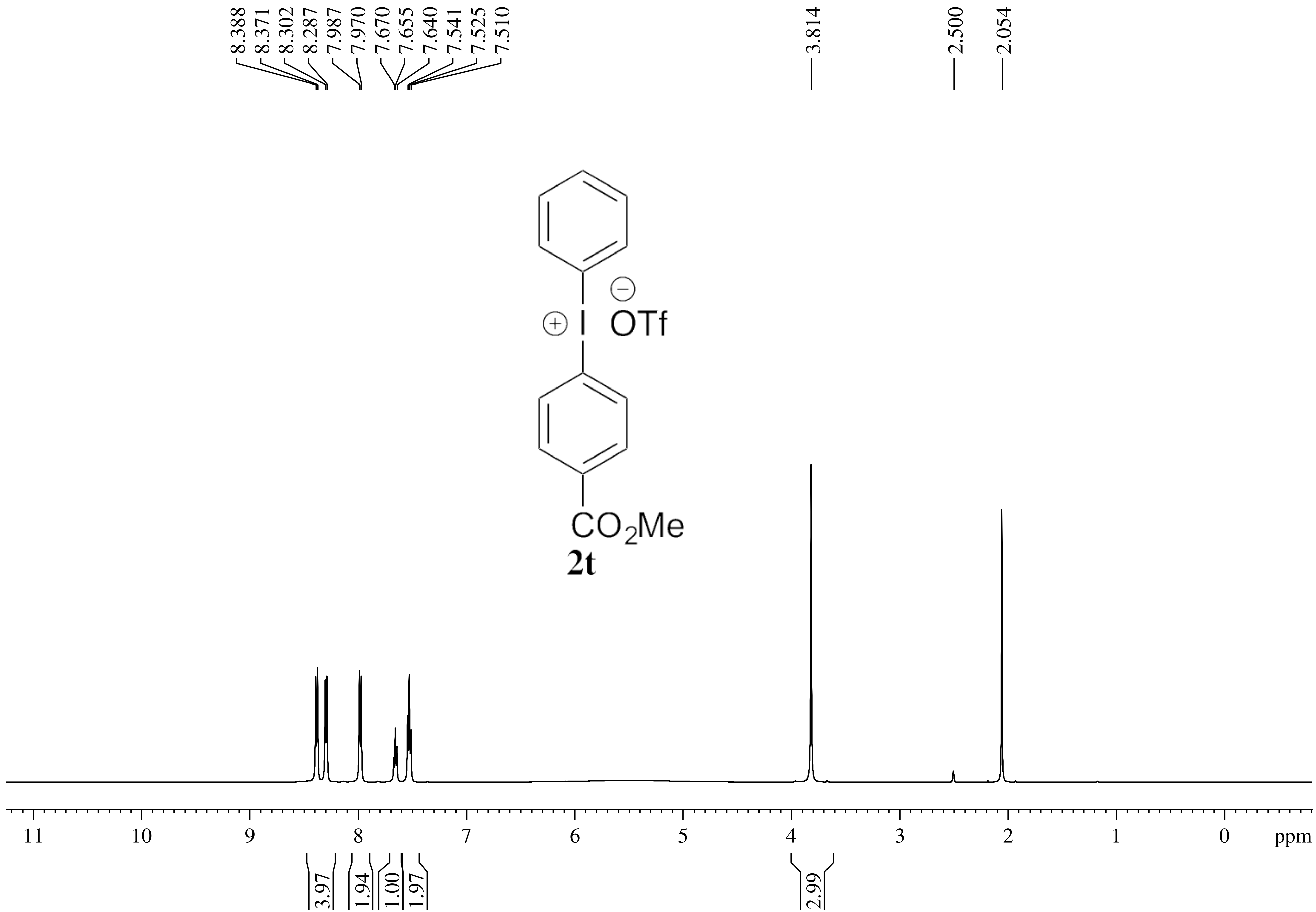


19F NMR, (CD3)2SO, 282 MHz

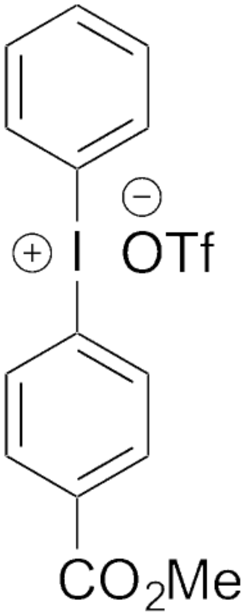


2s

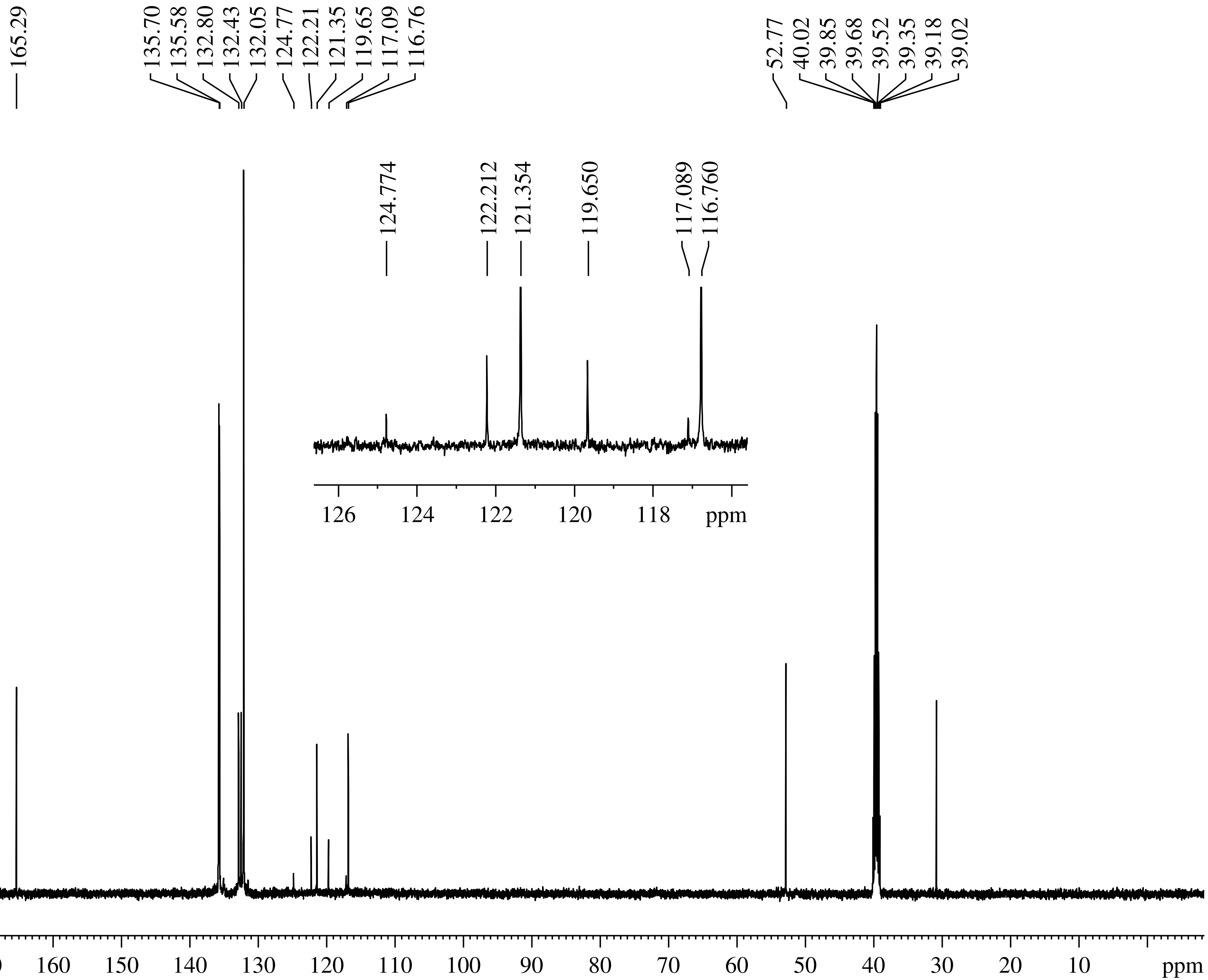
1H NMR, (CD3)2SO, 500 MHz



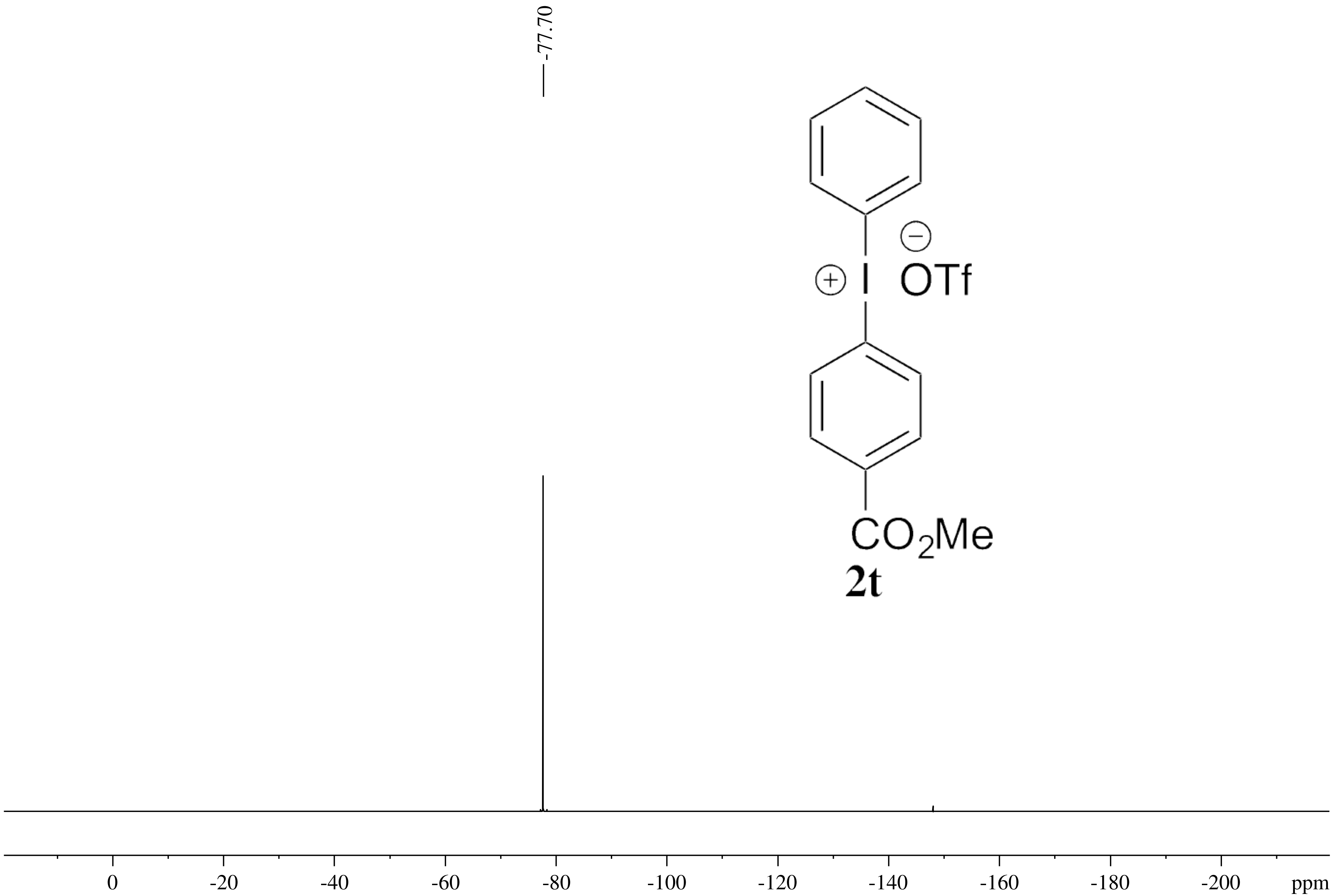
13C NMR, (CD3)2SO, 125 MHz



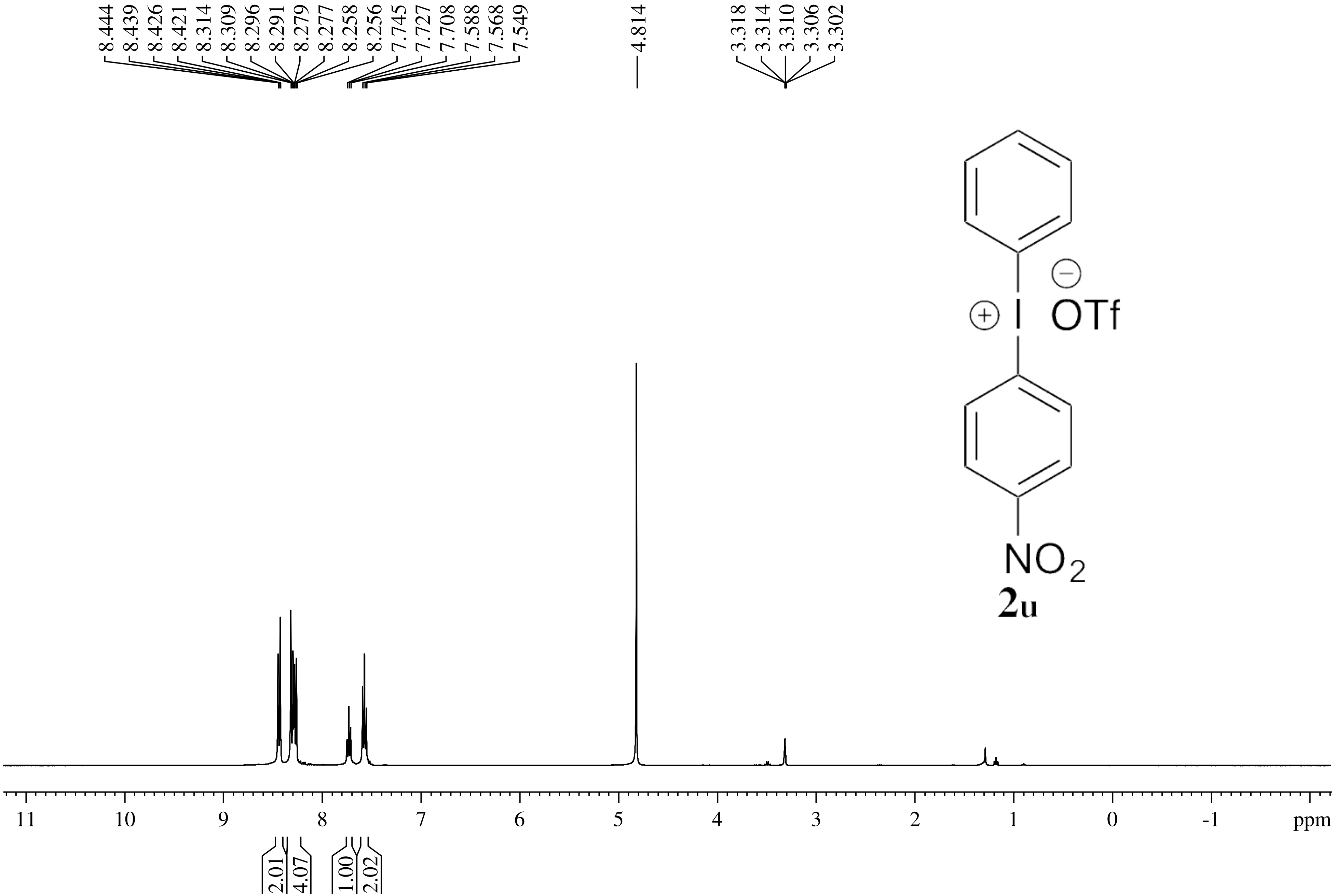
2t



19F NMR, (CD3)2SO, 376 MHz

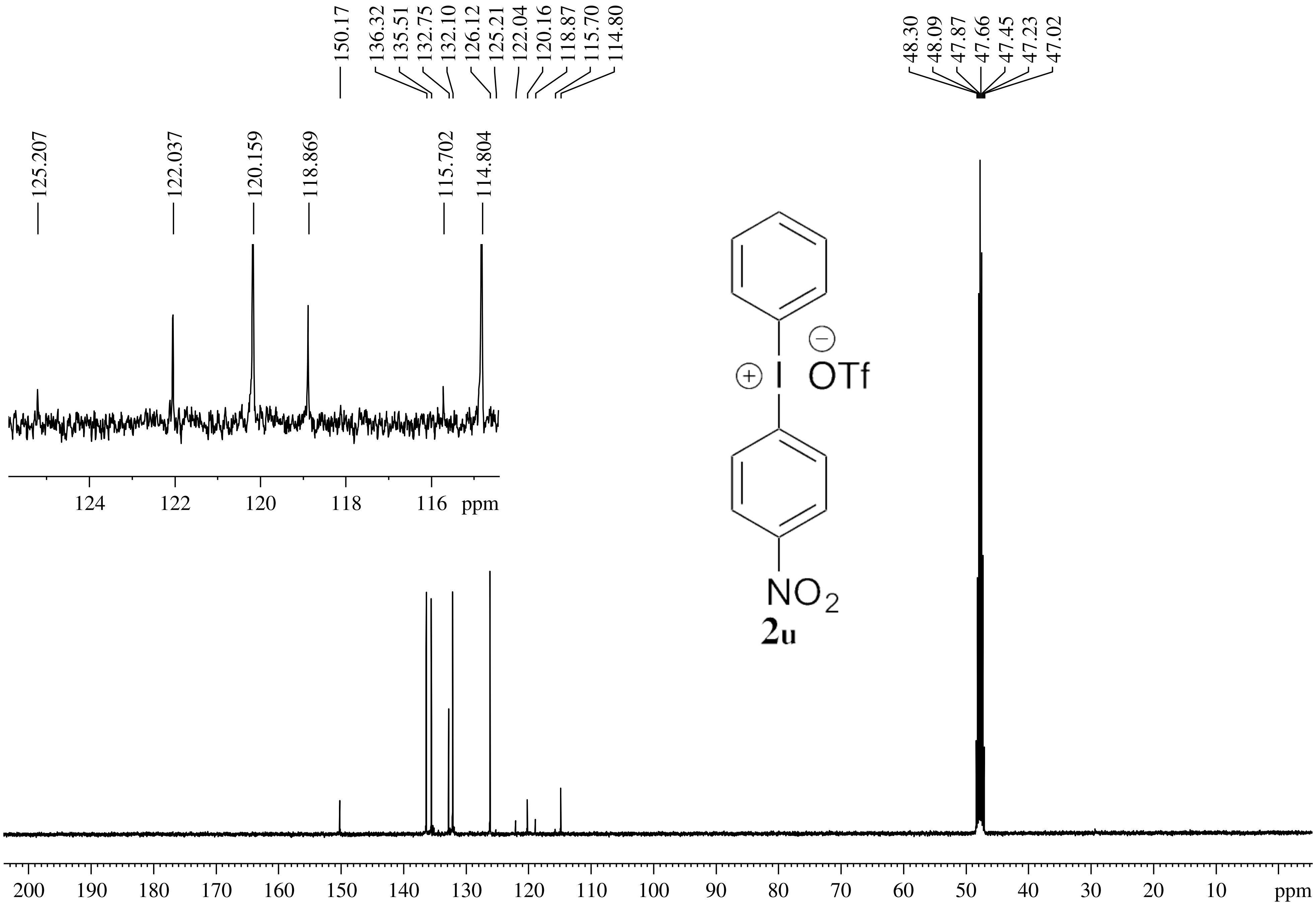


1H NMR, (CD3)2SO, 400 MHz

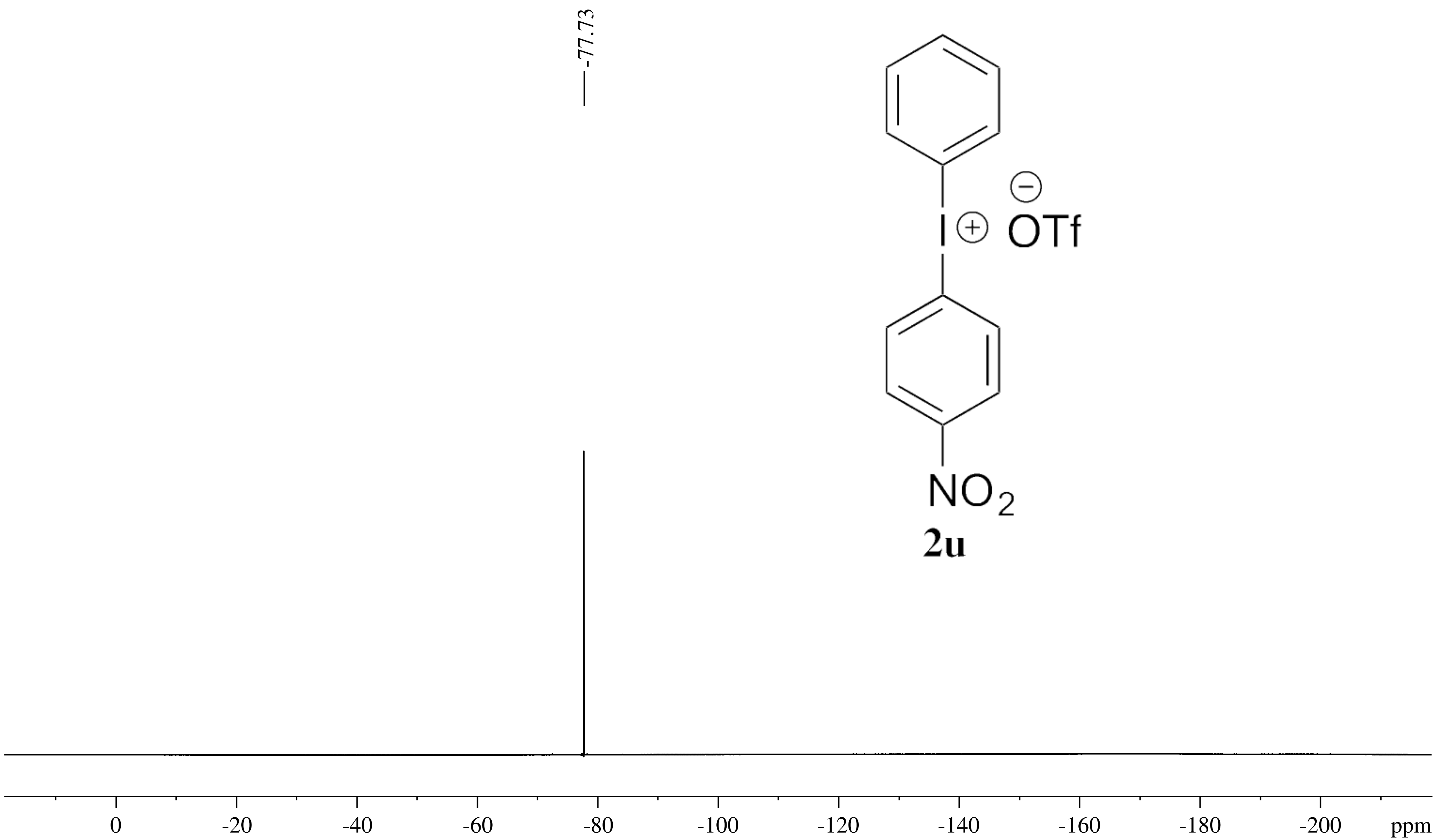


2u

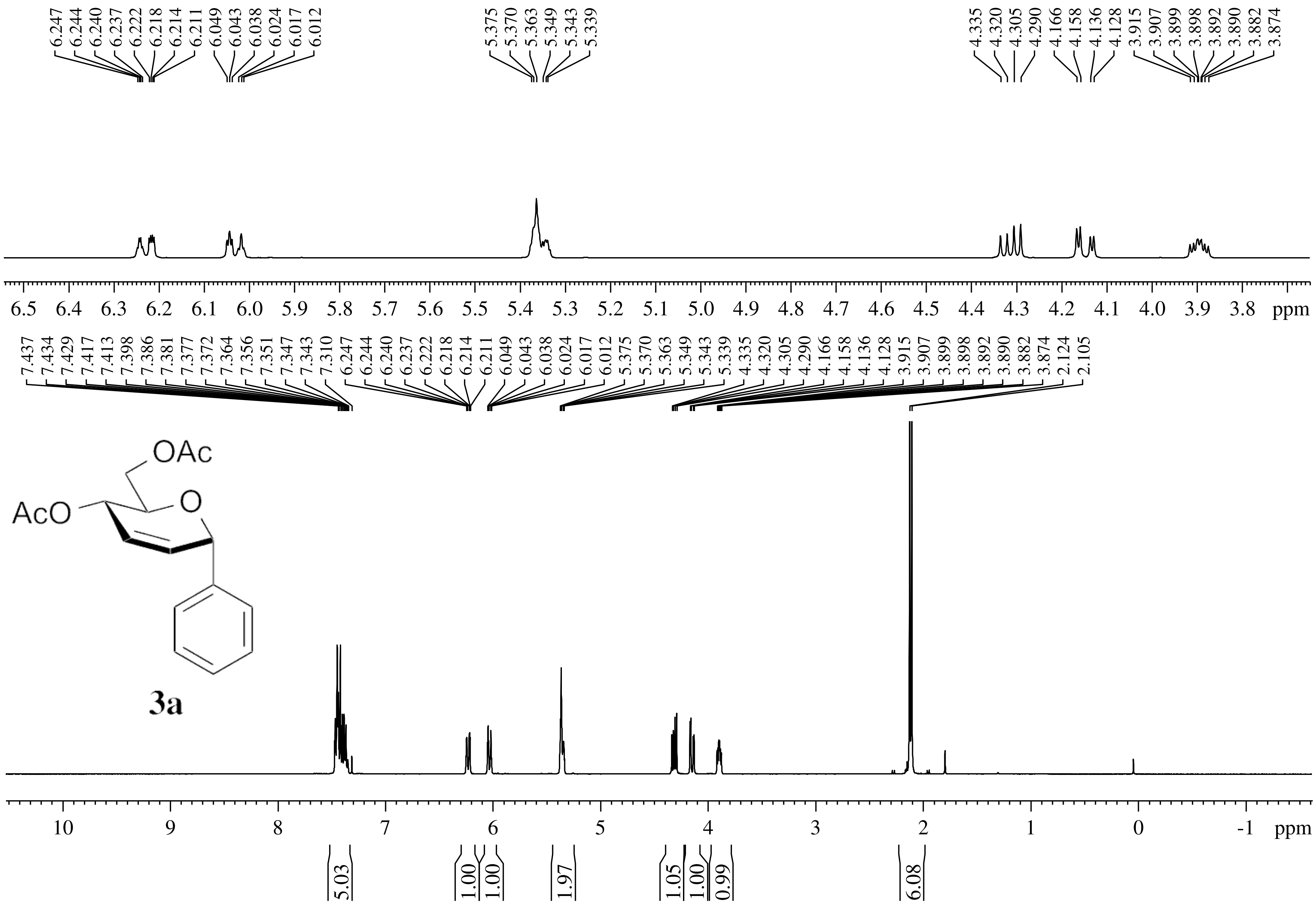
13C NMR, (CD3)2SO, 100 MHz



^{19}F NMR, (CD)$_3$SO, 376 MHz

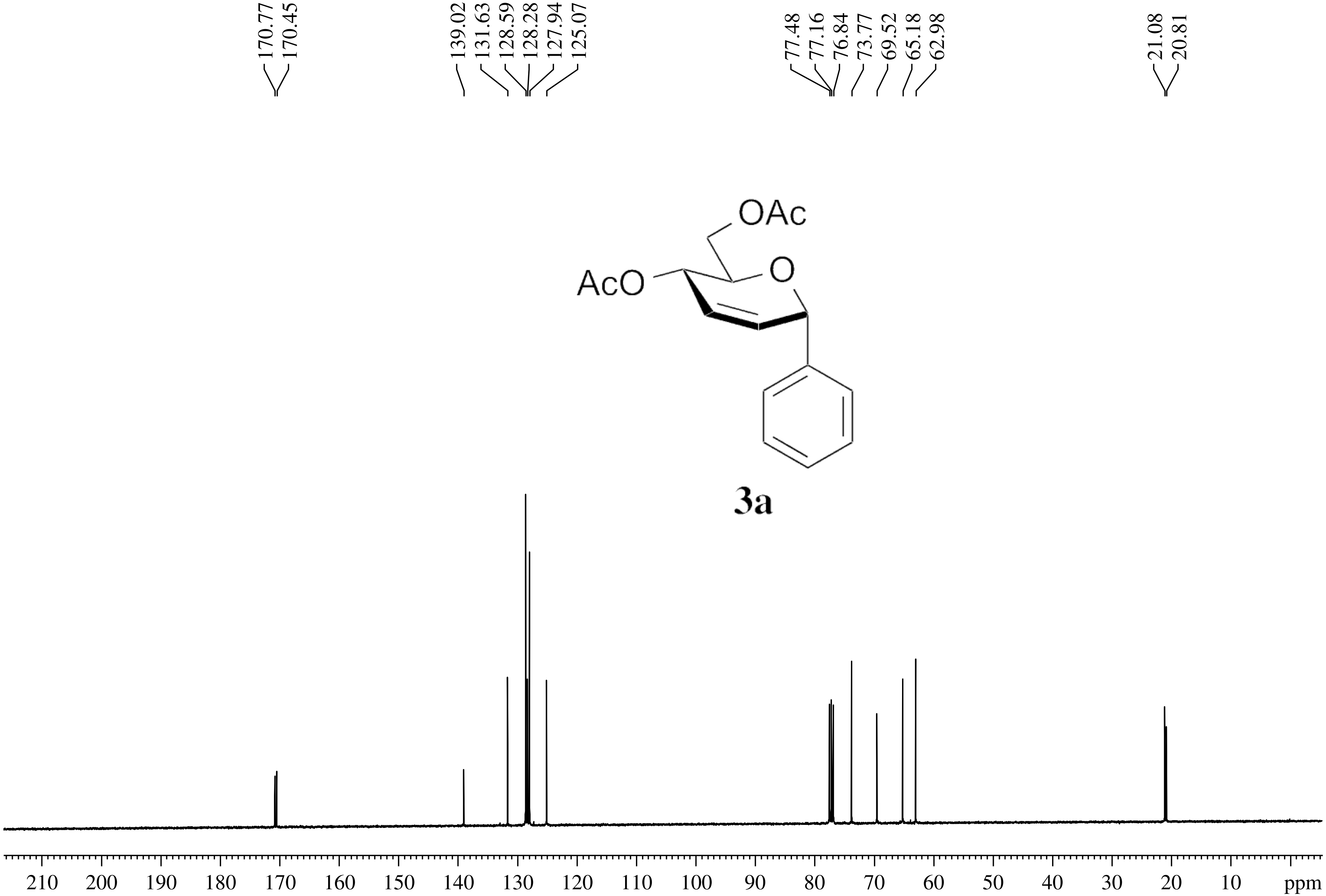


^1H NMR, $CDCl_3$, 400 MHz

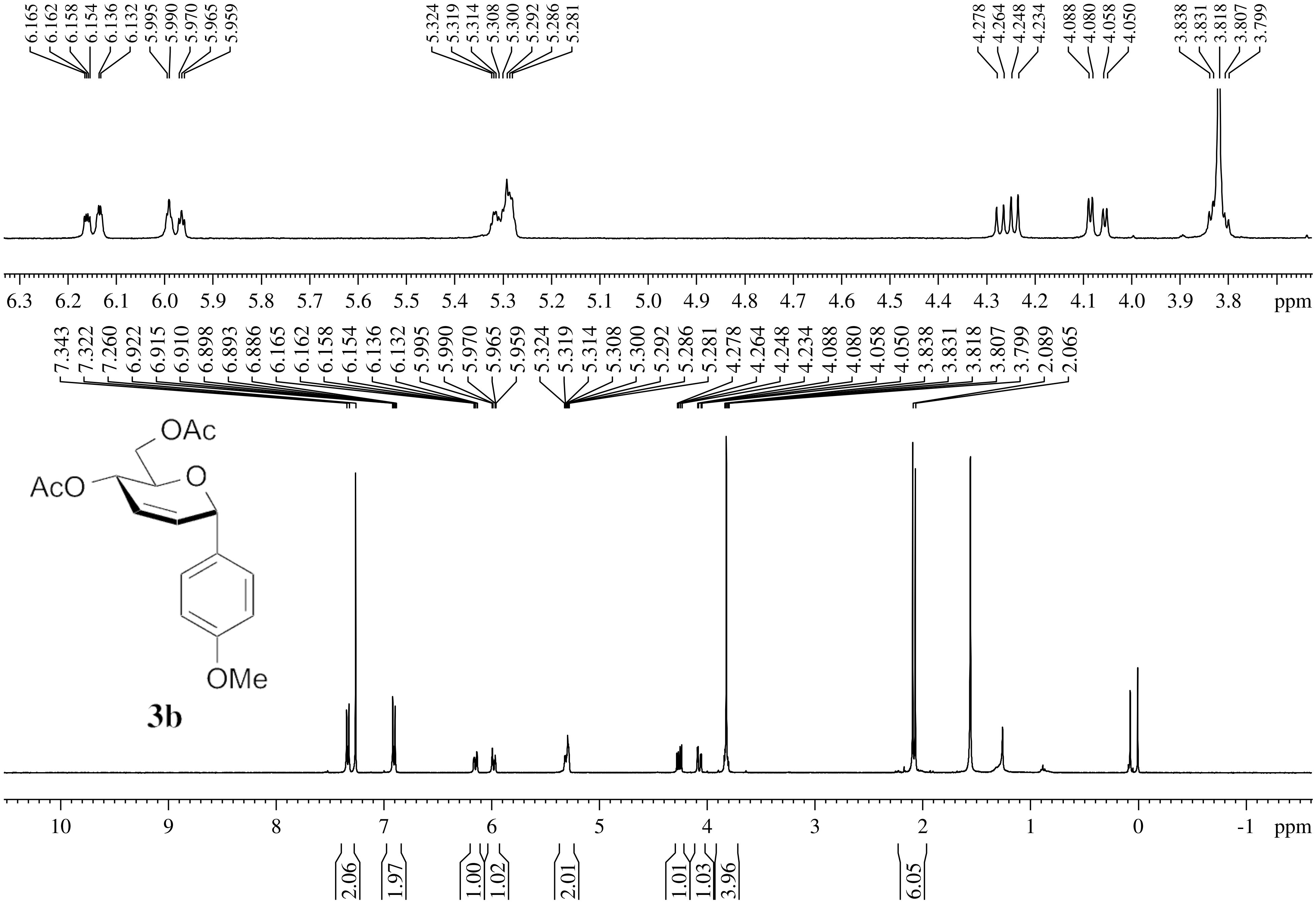


3a

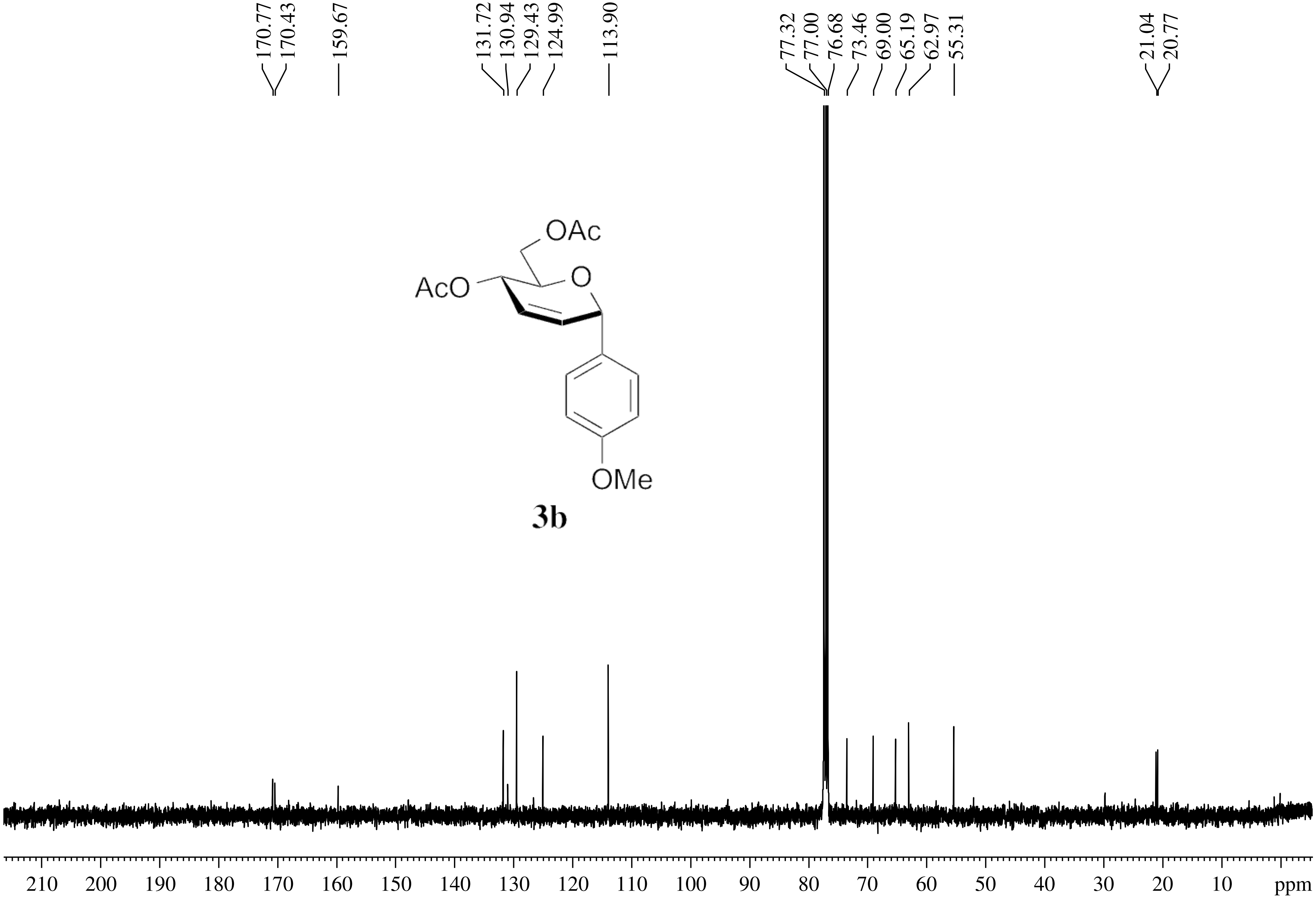
^{13}C NMR, $CDCl_3$, 100 MHz



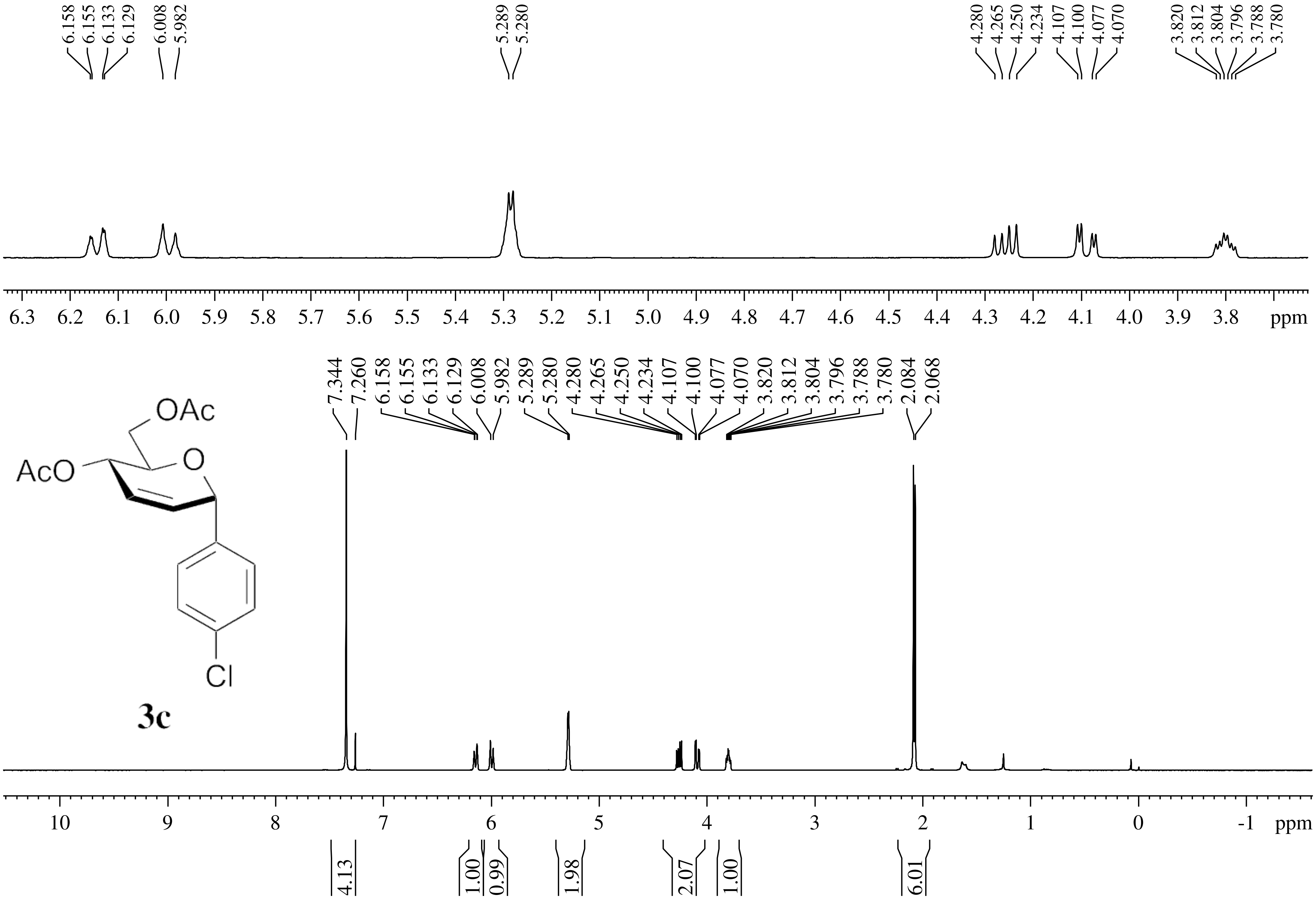
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, CDCl$_3$, 100 MHz

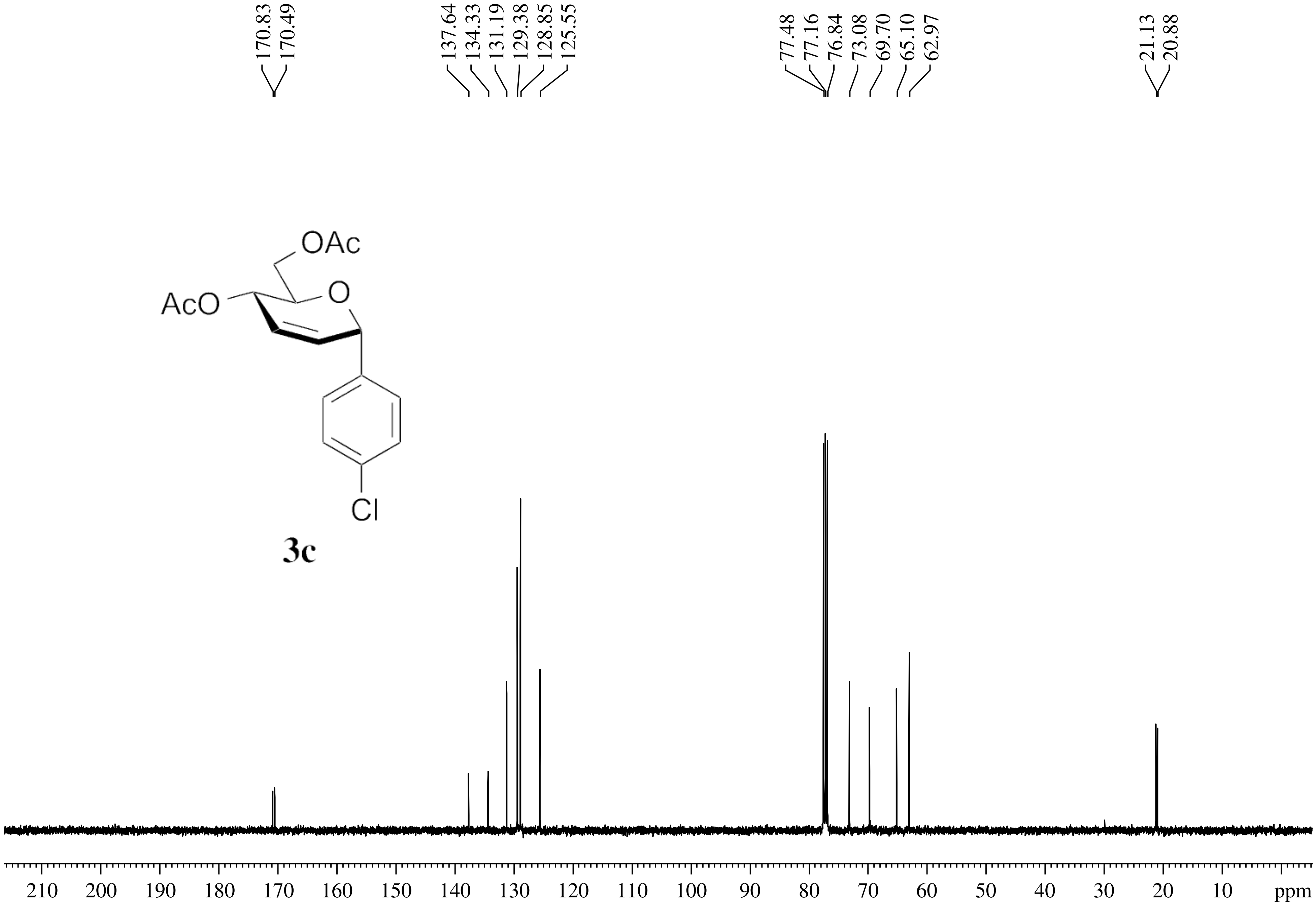


^{1}H NMR, $CDCl_3$, 400 MHz



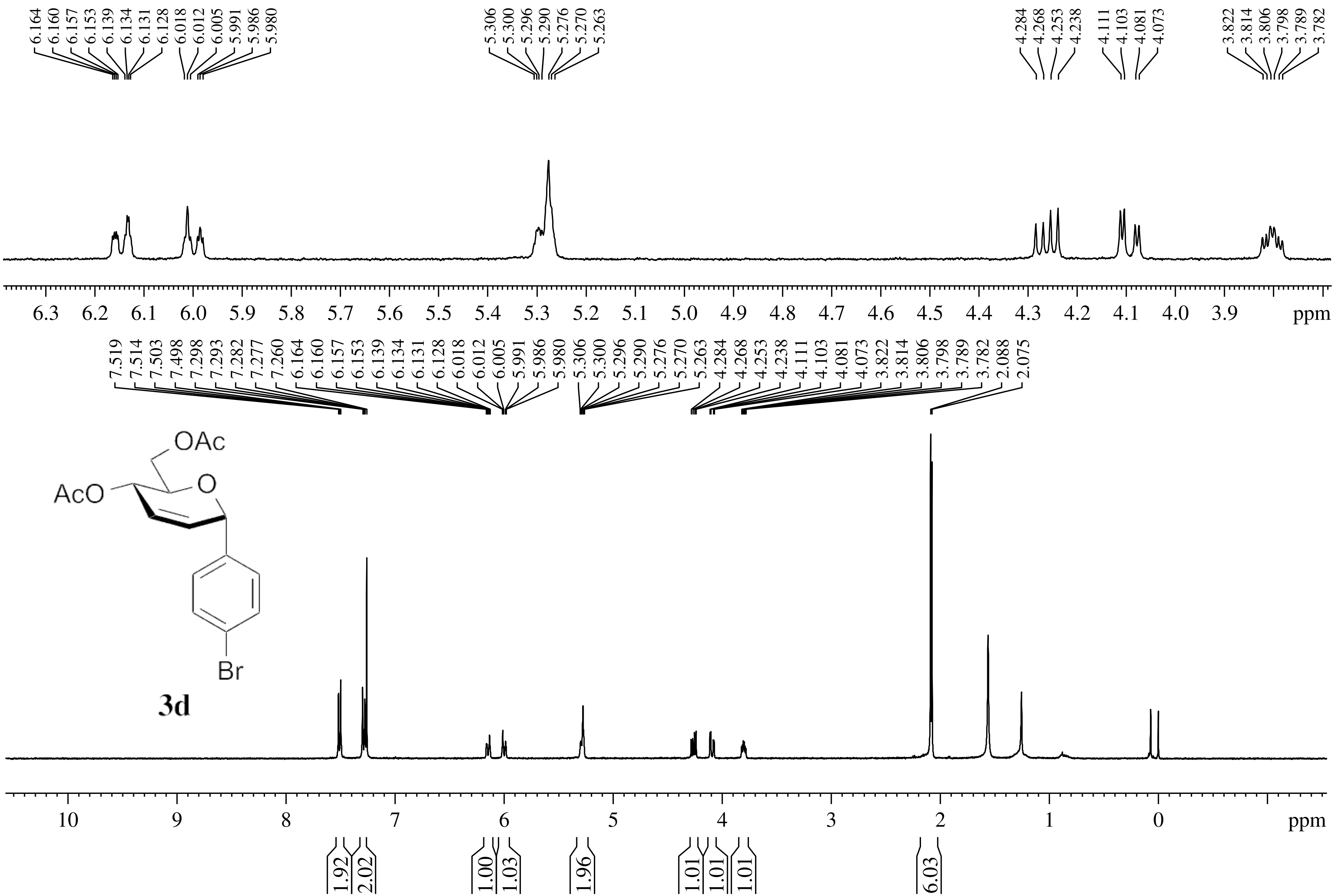
3c

^{13}C NMR, $CDCl_3$, 100 MHz



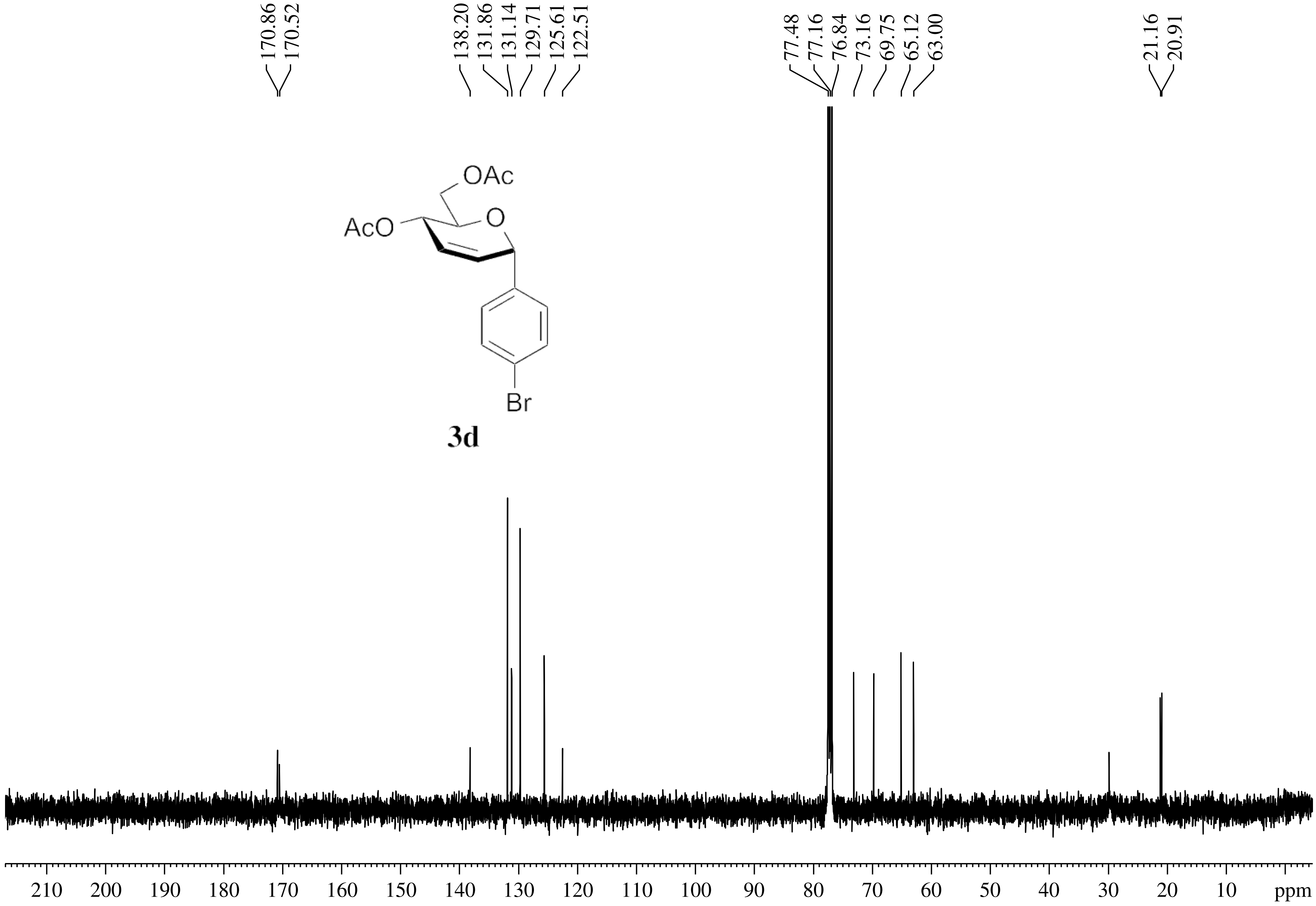
3c

^1H NMR, $CDCl_3$, 400 MHz

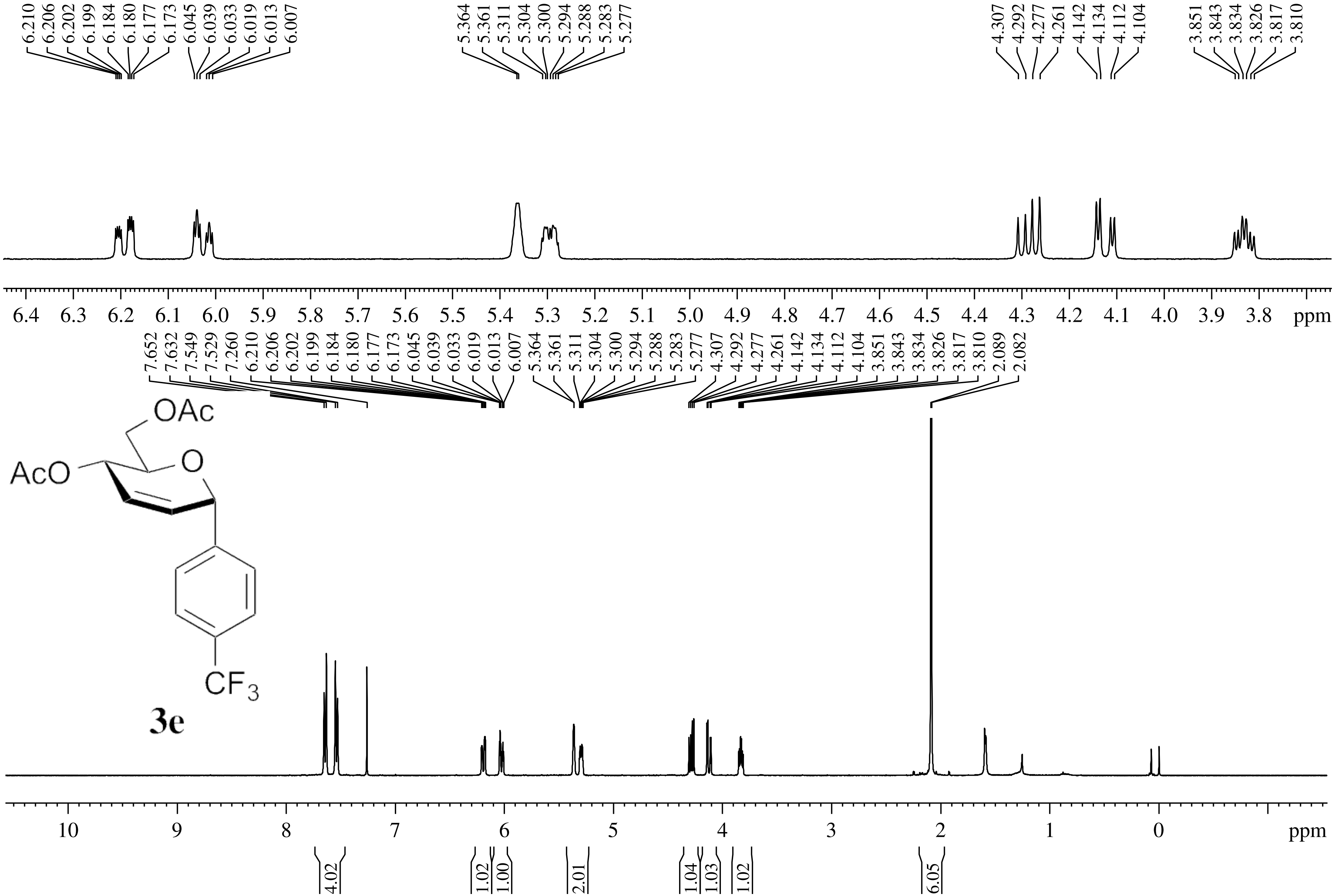


3d

^{13}C NMR, $CDCl_3$, 100 MHz

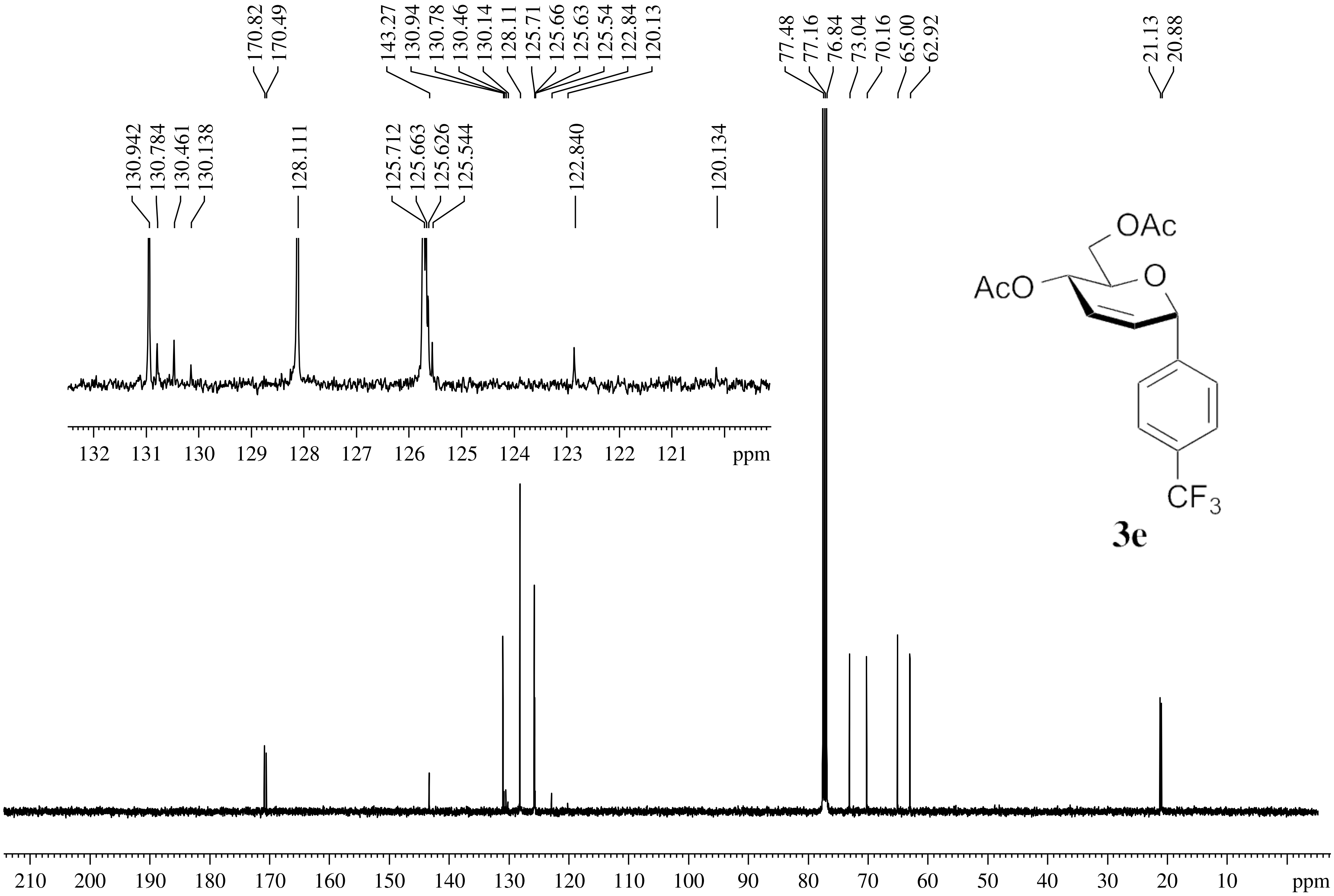


^{1}H NMR, $CDCl_3$, 400 MHz

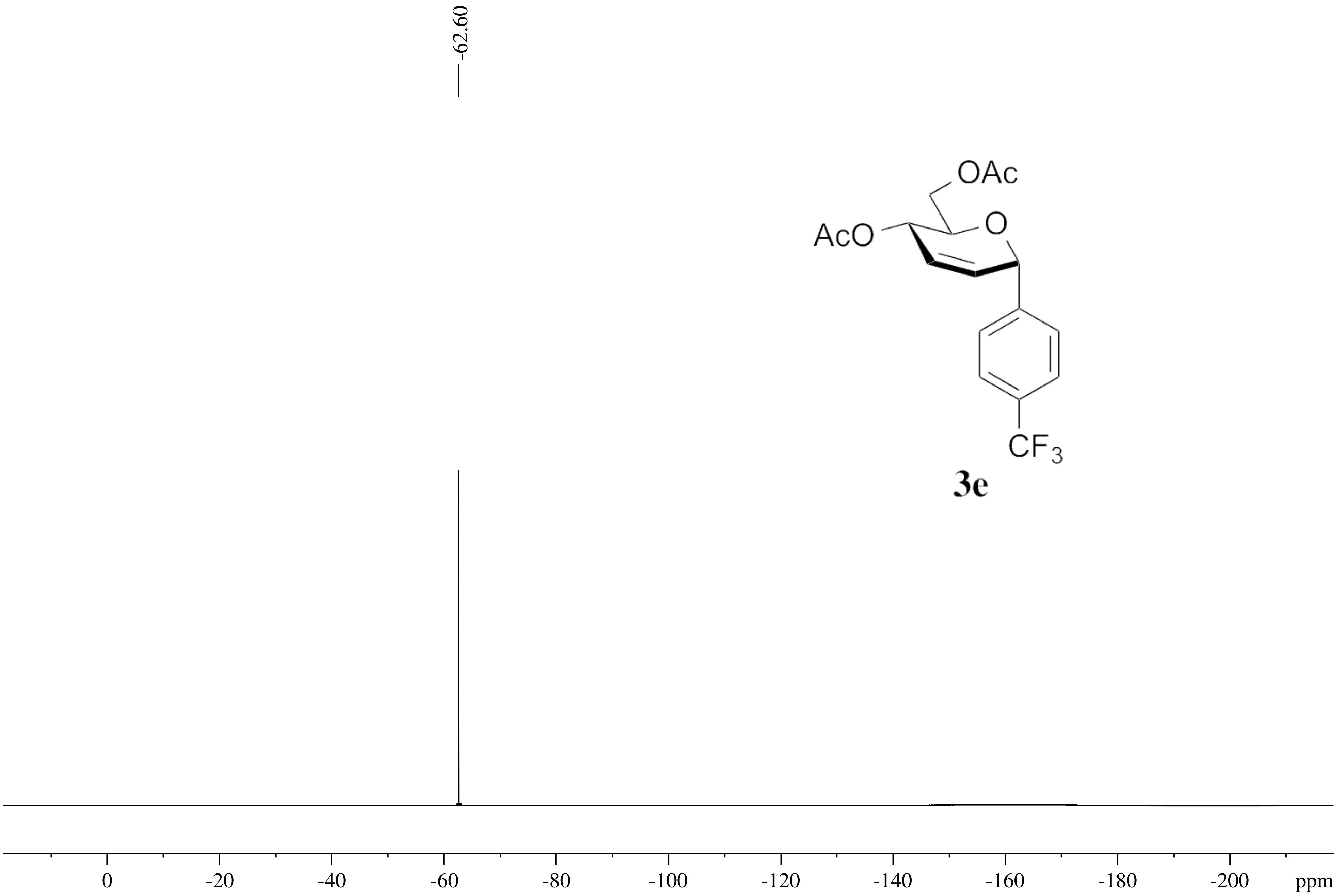


3e

^{13}C NMR, $CDCl_3$, 100 MHz

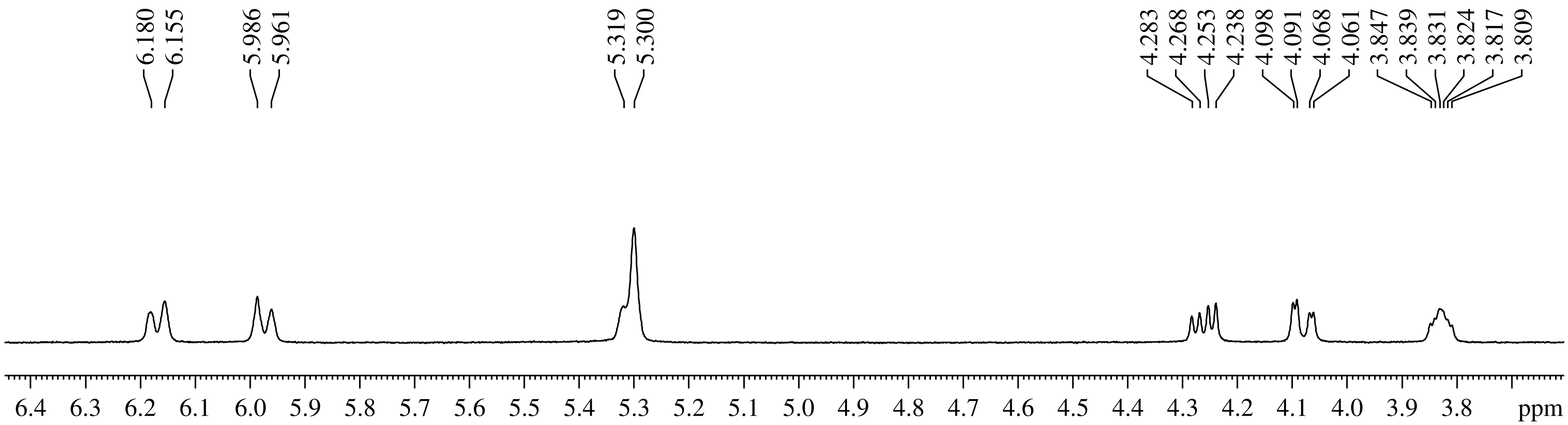


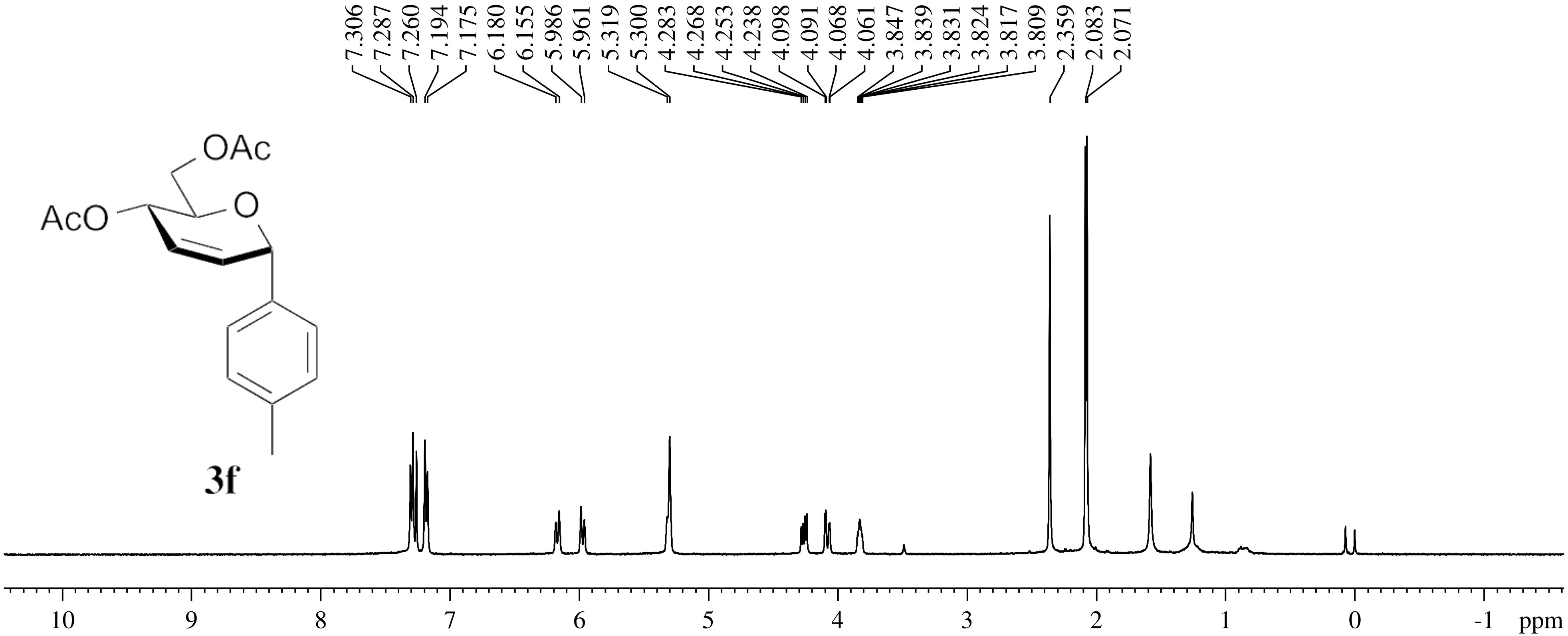
^{19}F NMR, $CDCl_3$, 376 MHz



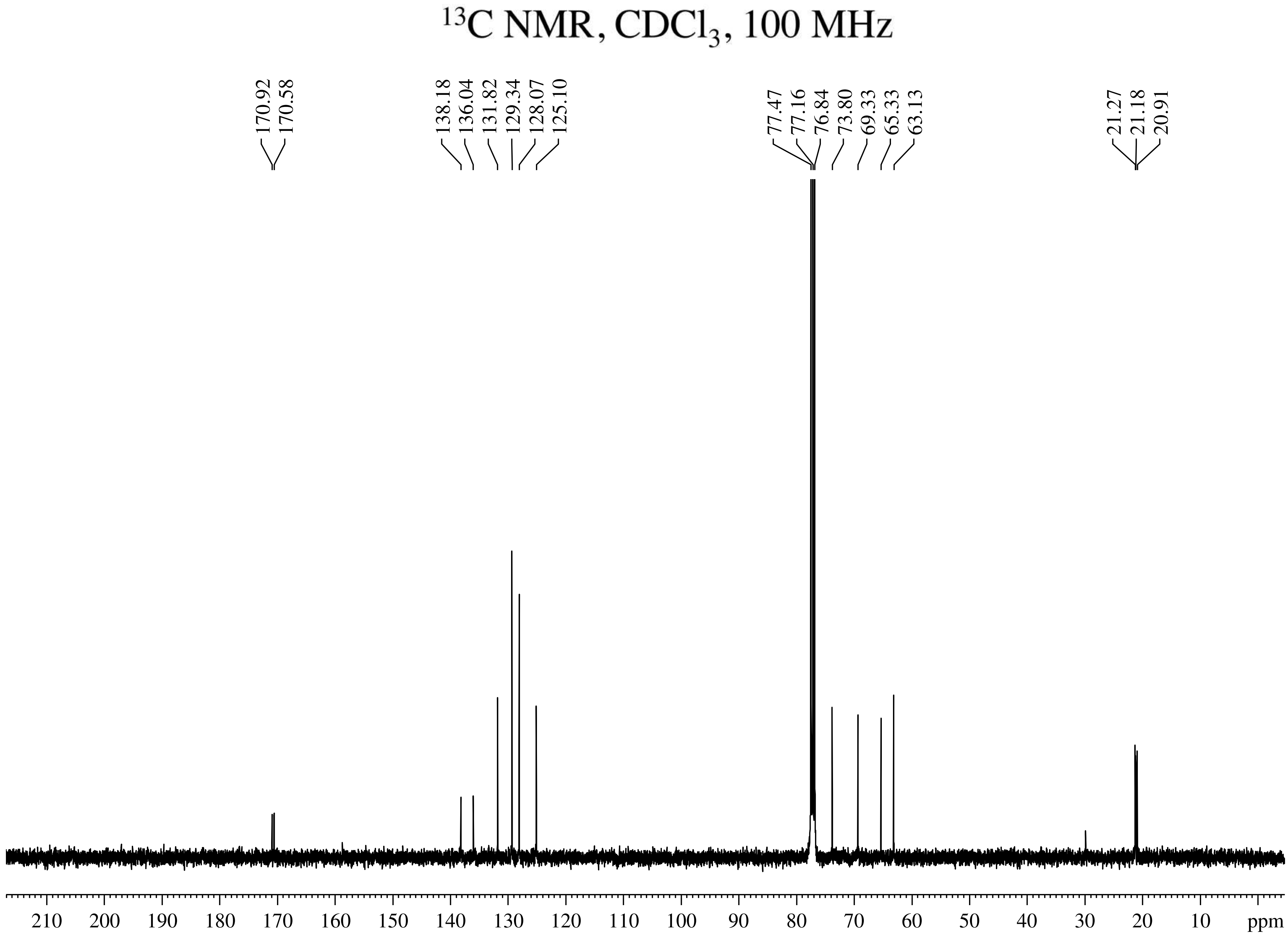
3e

^1H NMR, $CDCl_3$, 400 MHz

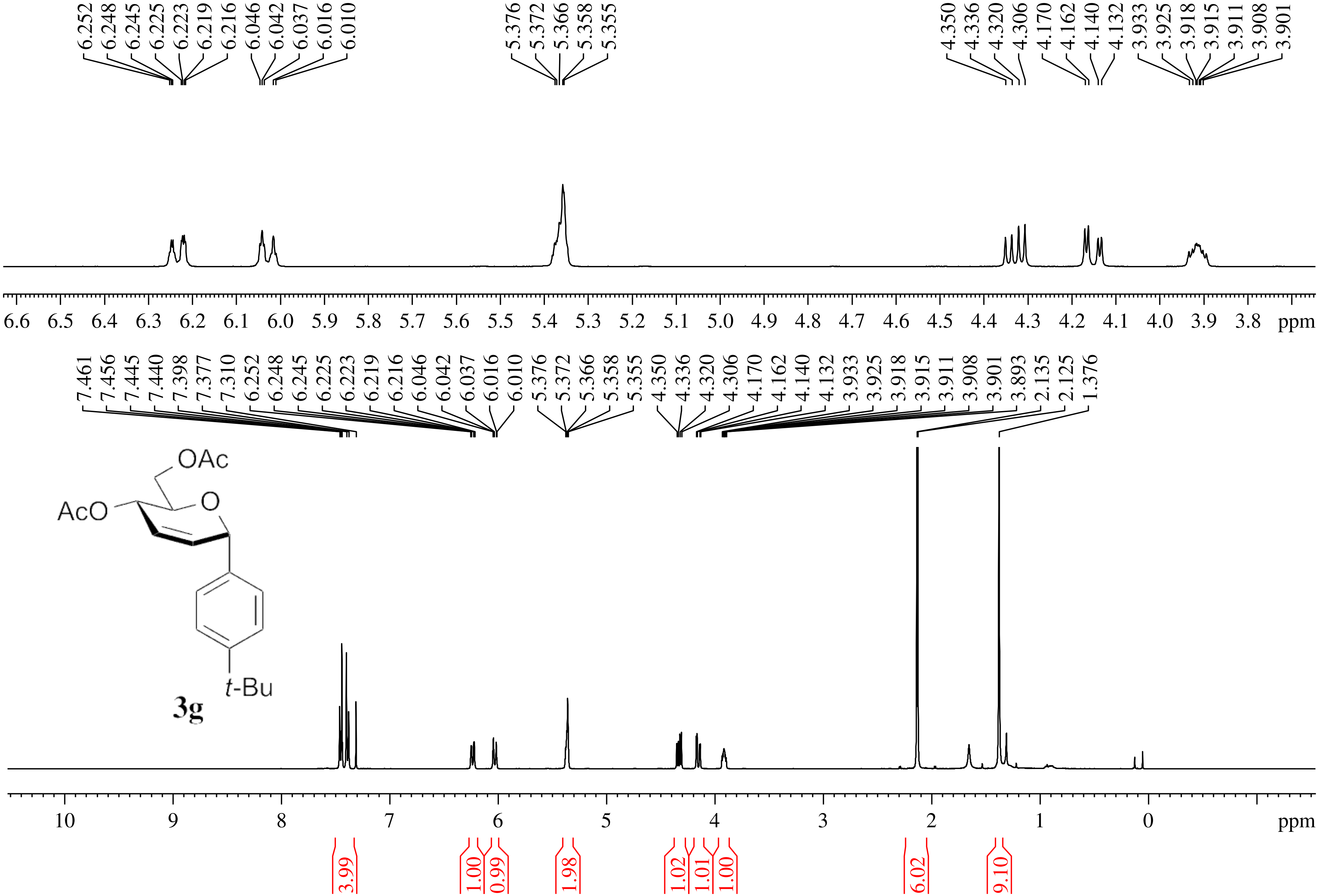




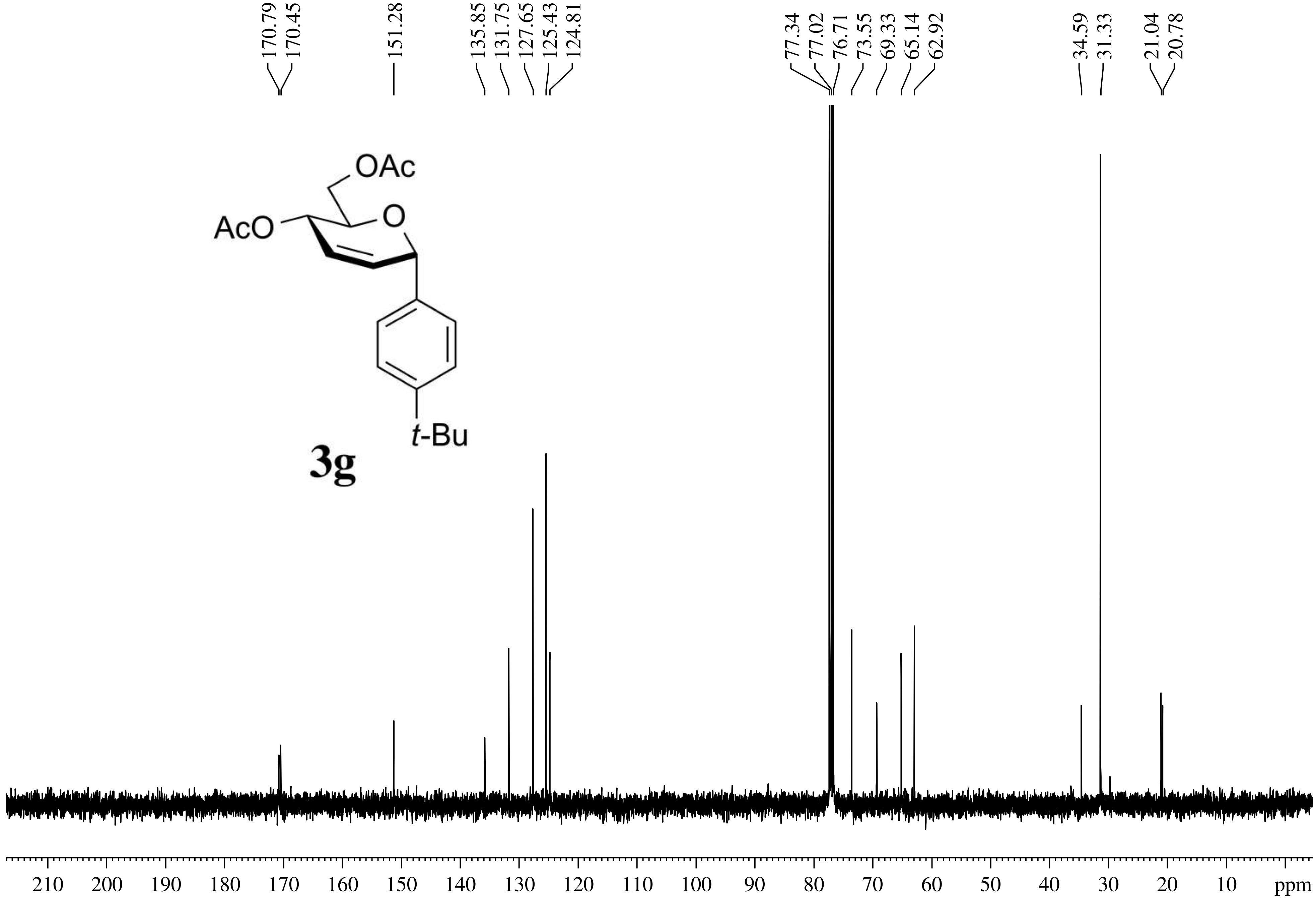
3f


13C NMR, CDCl3, 100 MHz
170.92
170.58
138.18
136.04
131.82
129.34
128.07
125.10
77.47
77.16
76.84
73.80
69.33
65.33
63.13
21.27
21.18
20.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

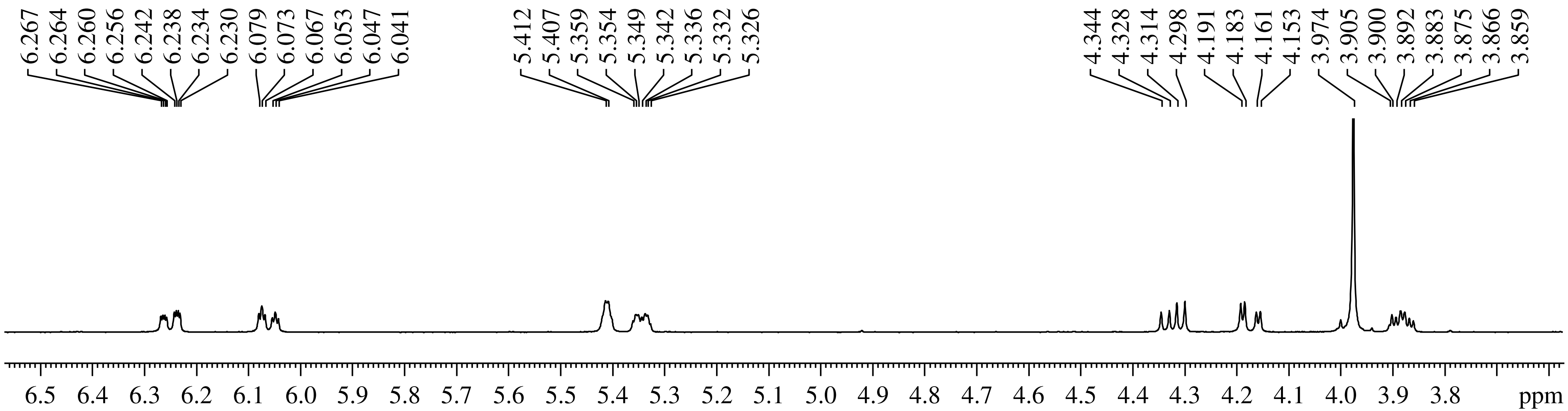
1H NMR, CDCl3, 400 MHz

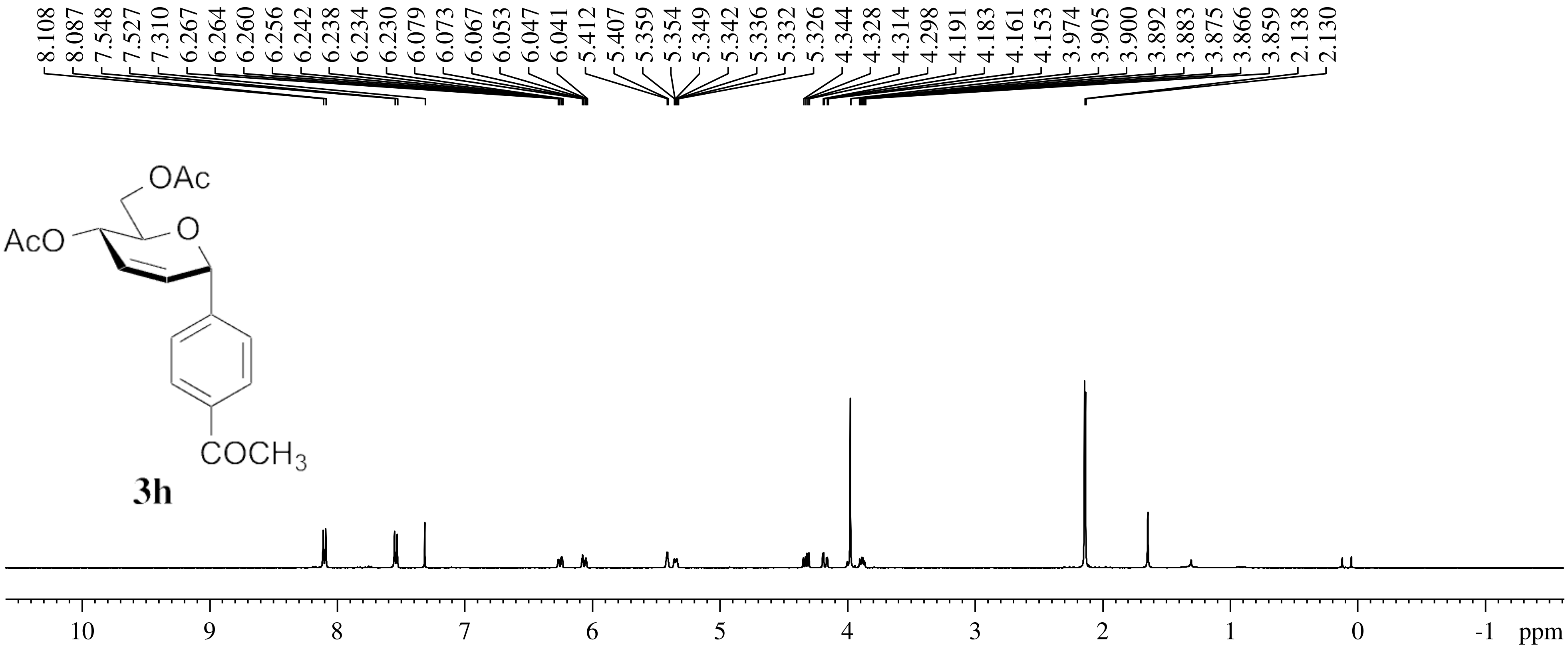


13C NMR, CDCl3, 100 MHz



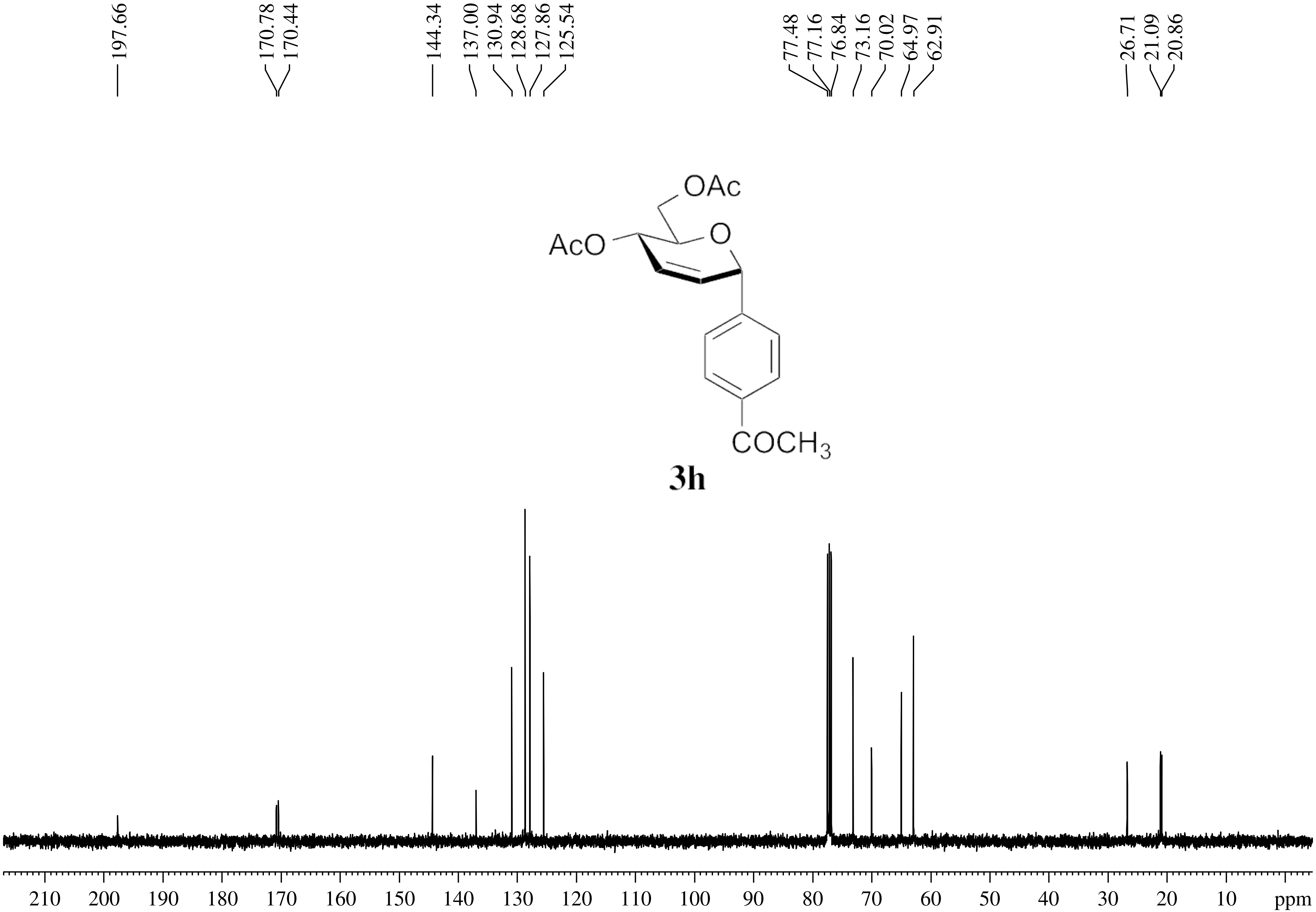
1H NMR, CDCl3, 400 MHz



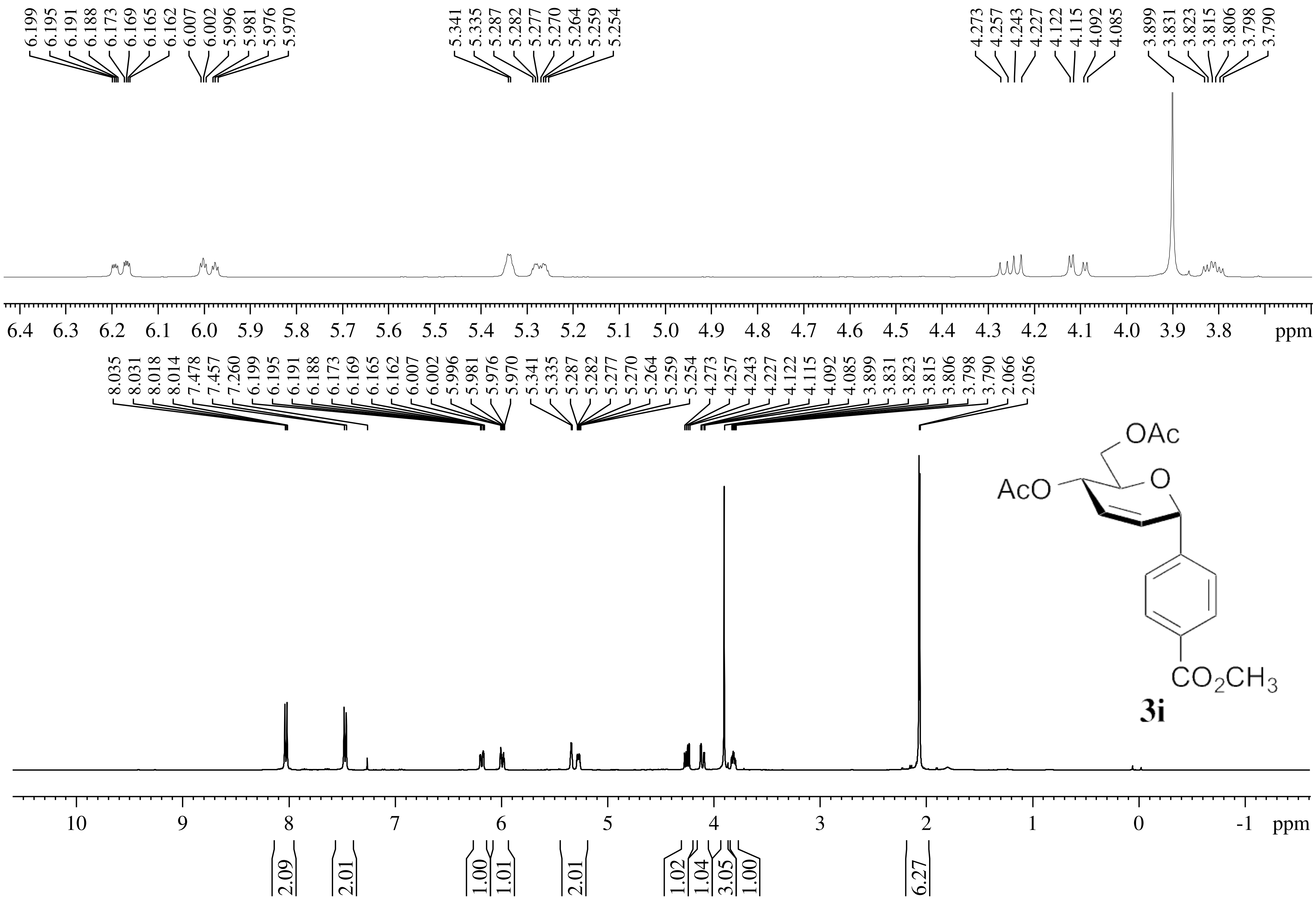


3h

1H NMR, CDCl3, 400 MHz

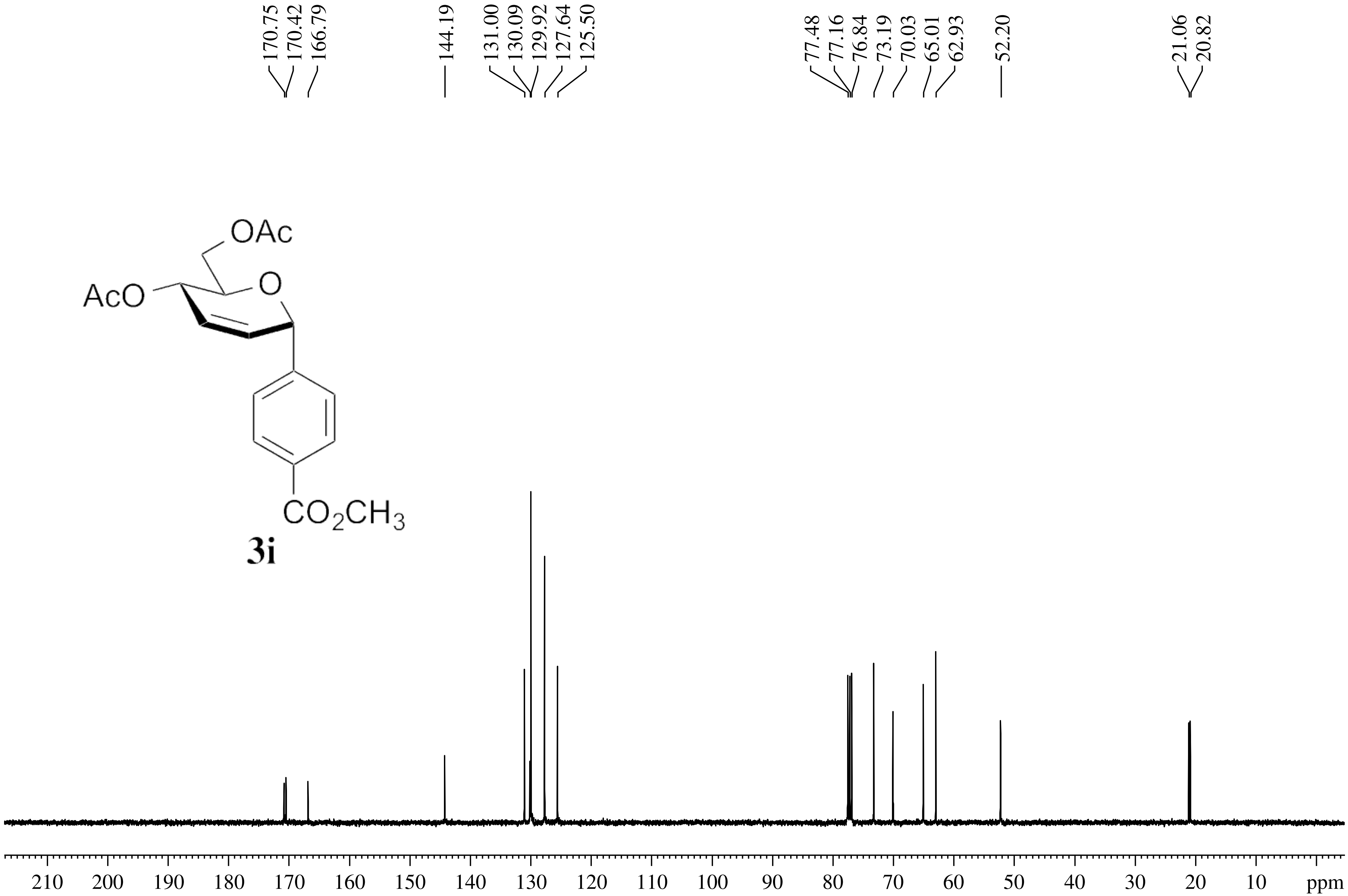


1H NMR, CDCl3, 400 MHz

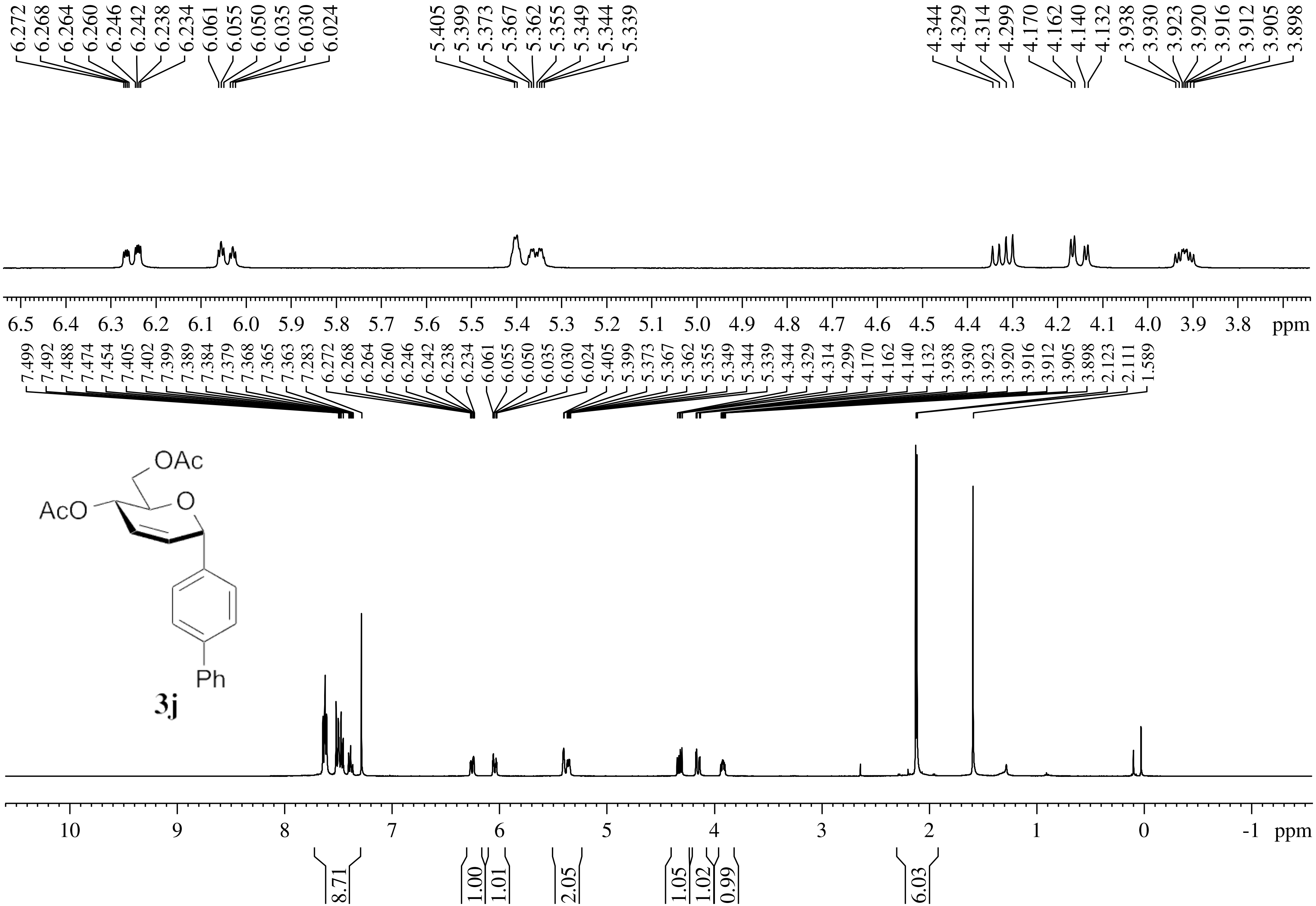


3i

1H NMR, CDCl3, 400 MHz

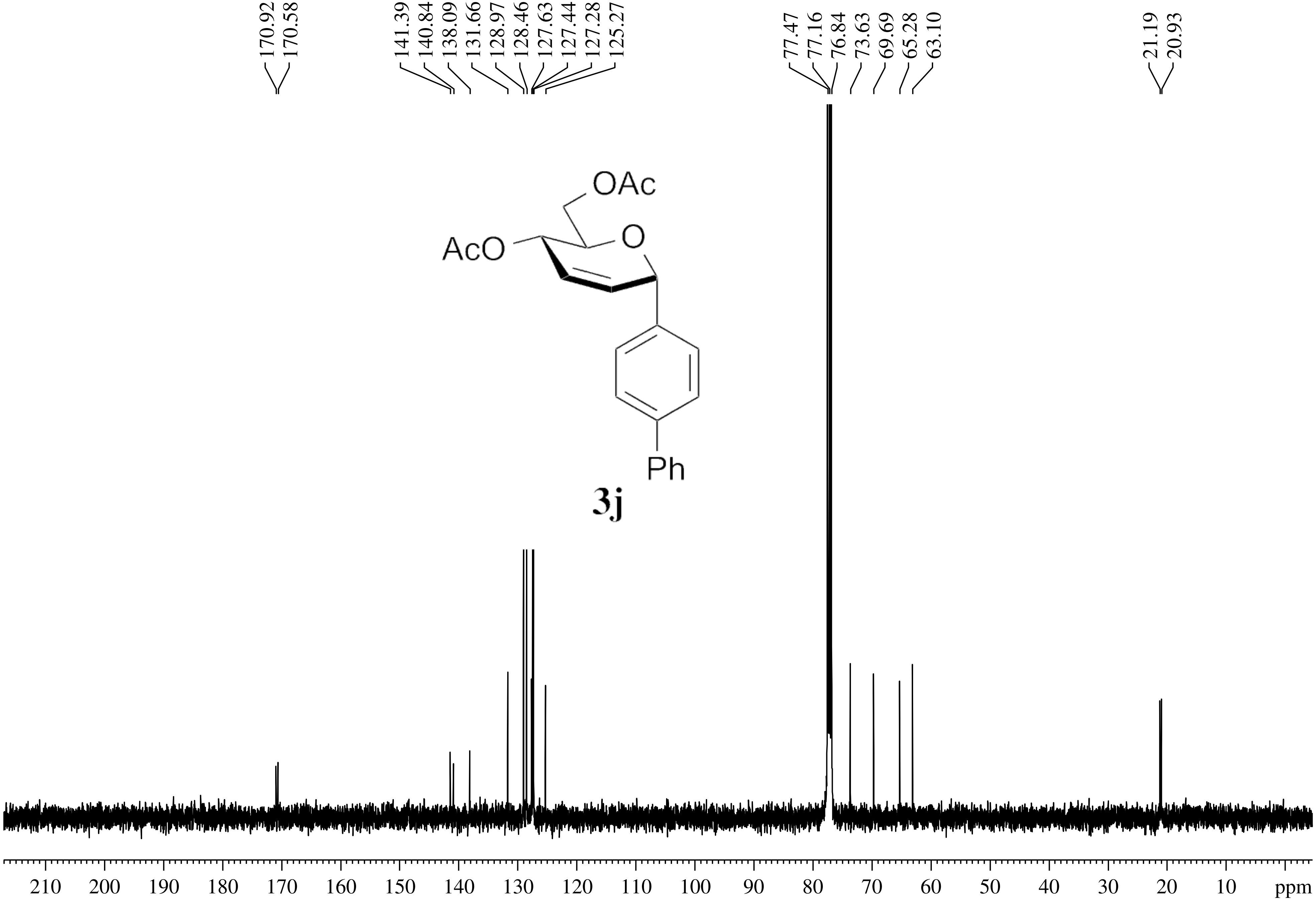


1H NMR, CDCl3, 400 MHz

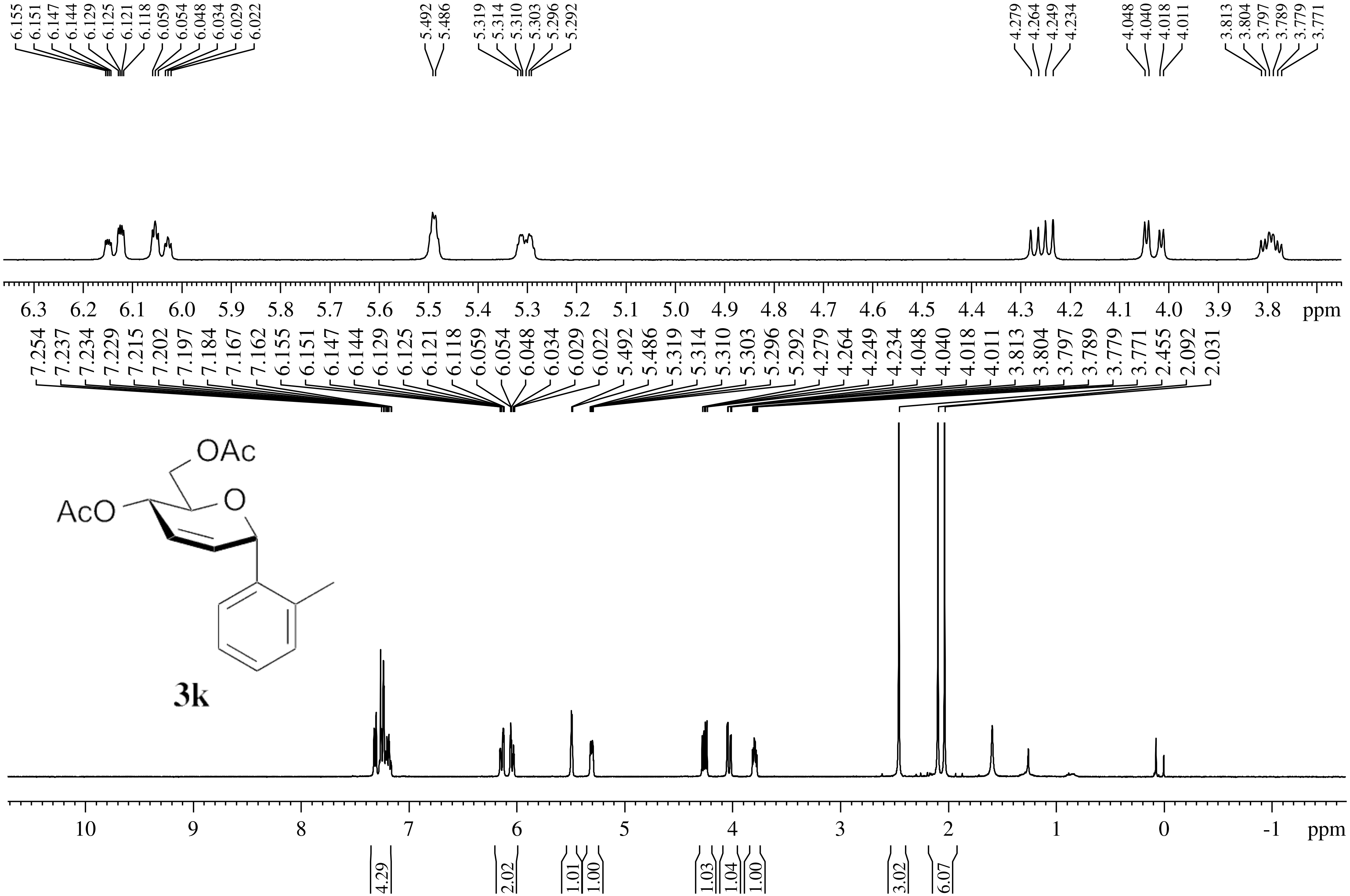


3j

1H NMR, CDCl3, 400 MHz

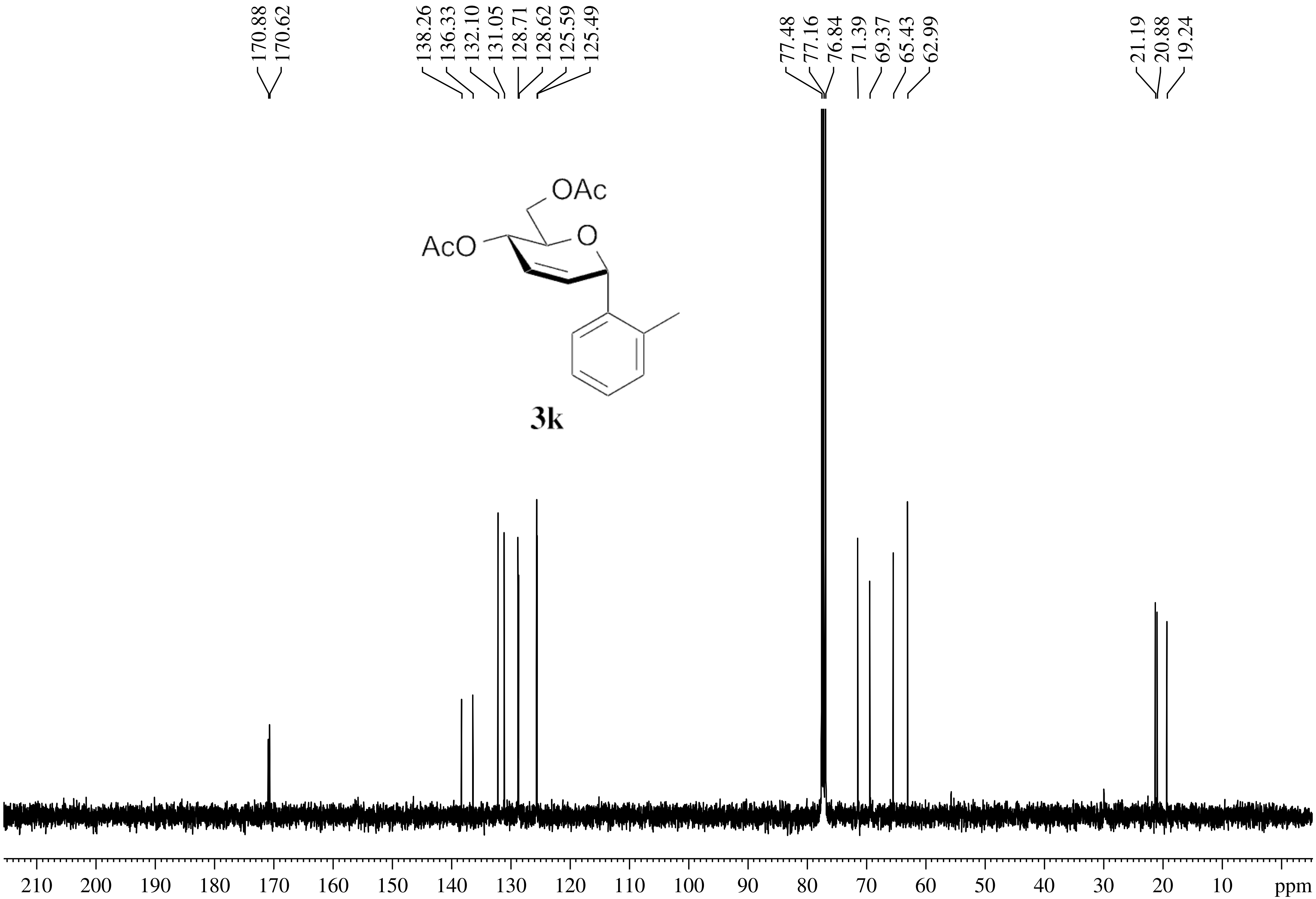


1H NMR, CDCl3, 400 MHz

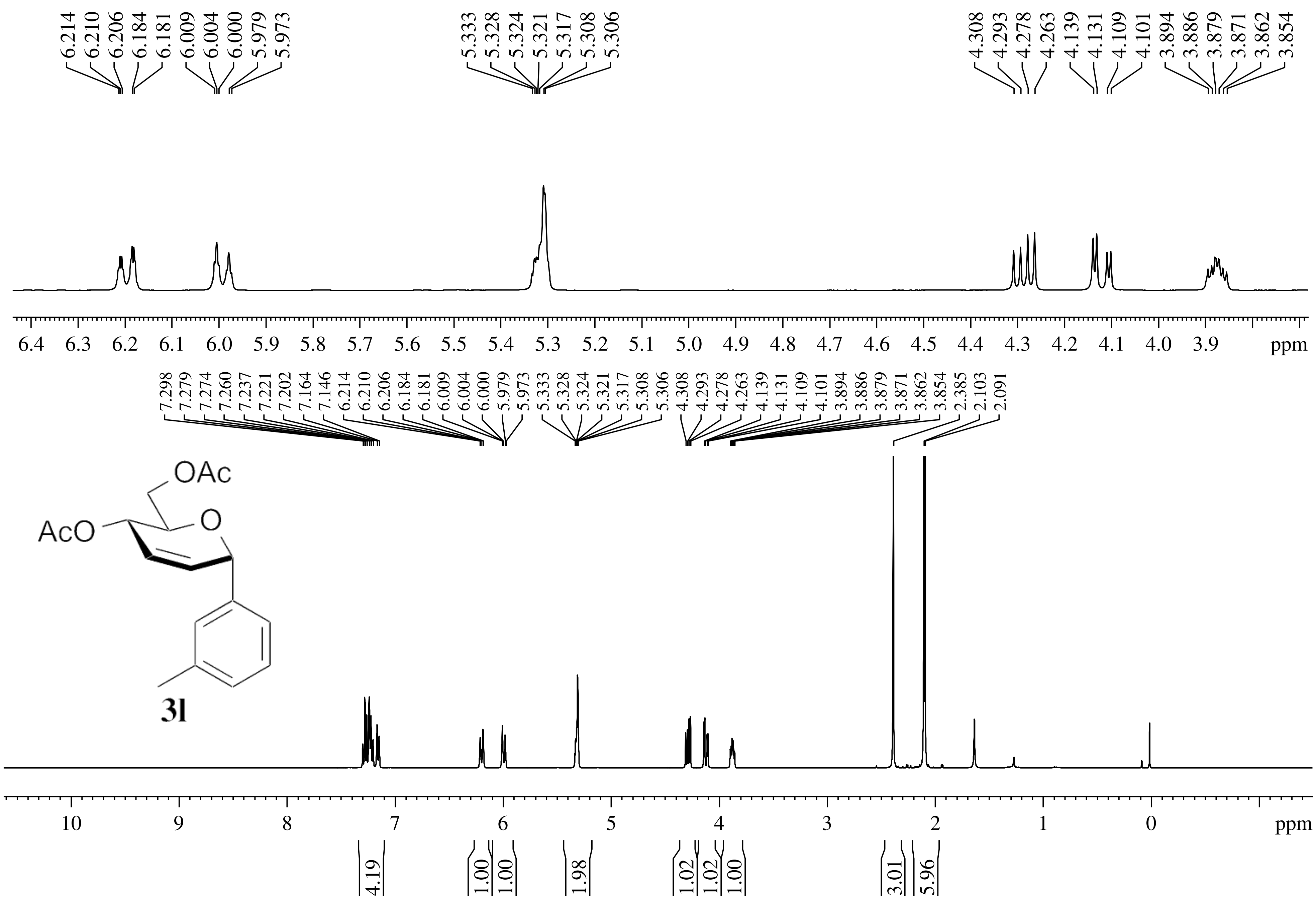


3k

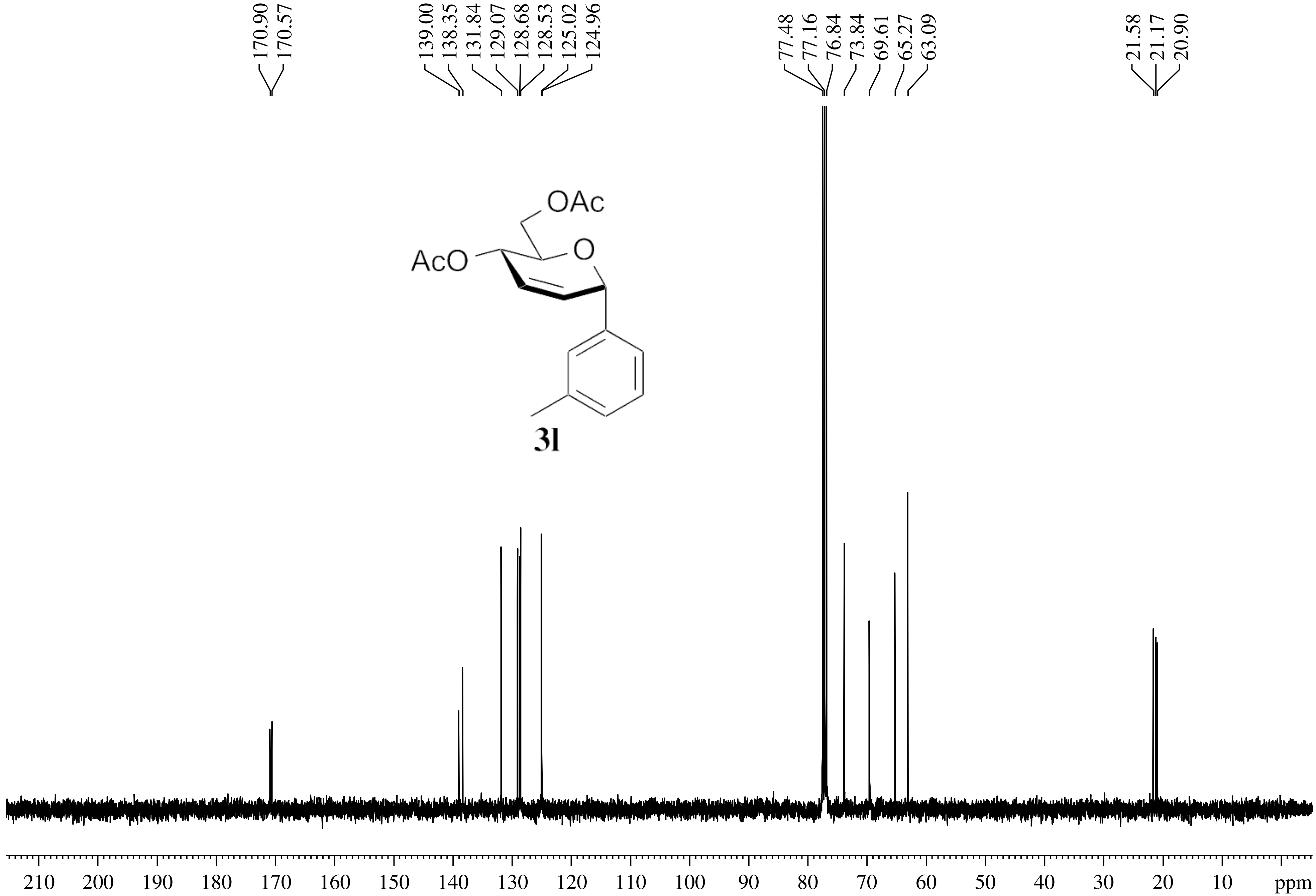
1H NMR, CDCl3, 400 MHz



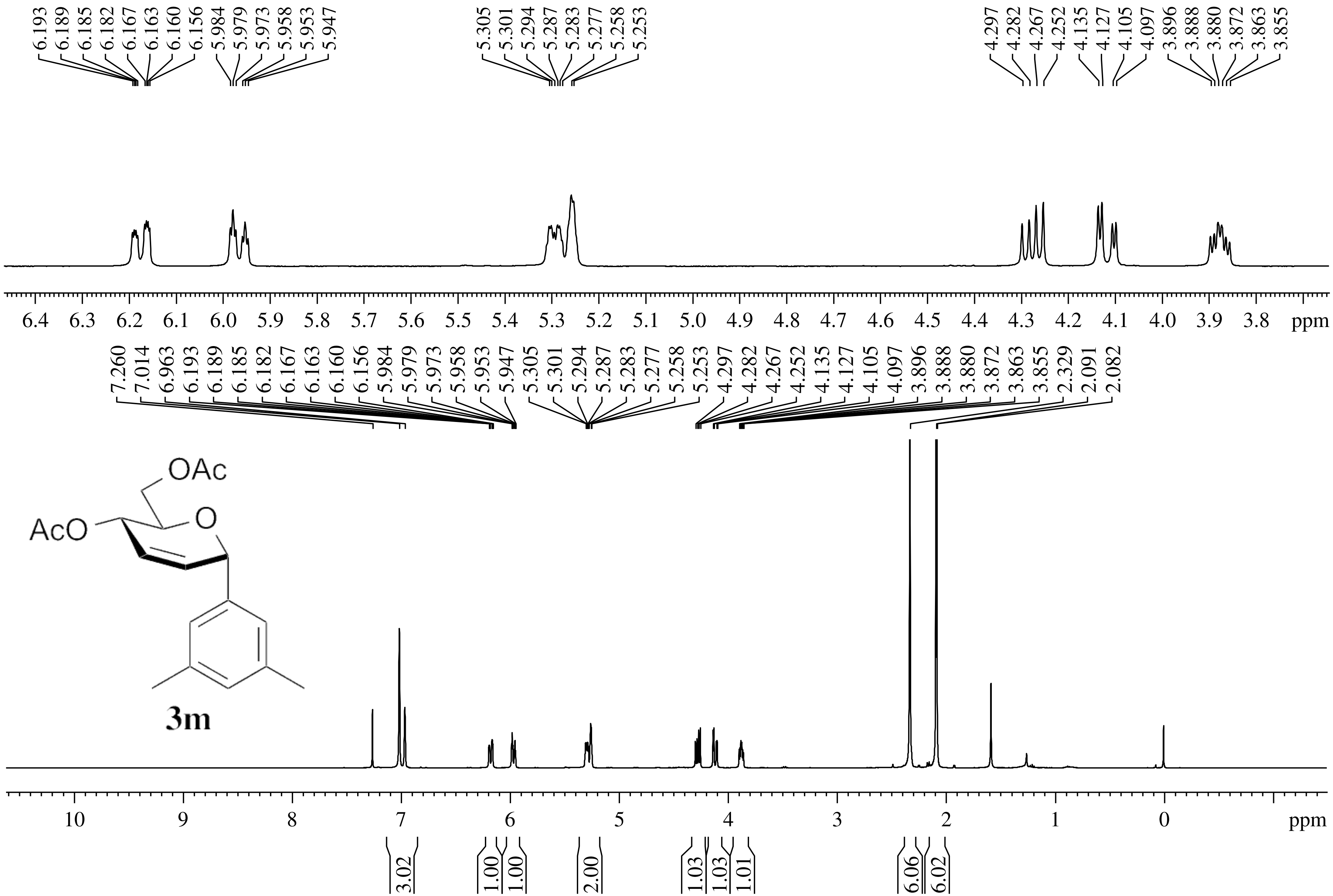
1H NMR, CDCl3, 400 MHz



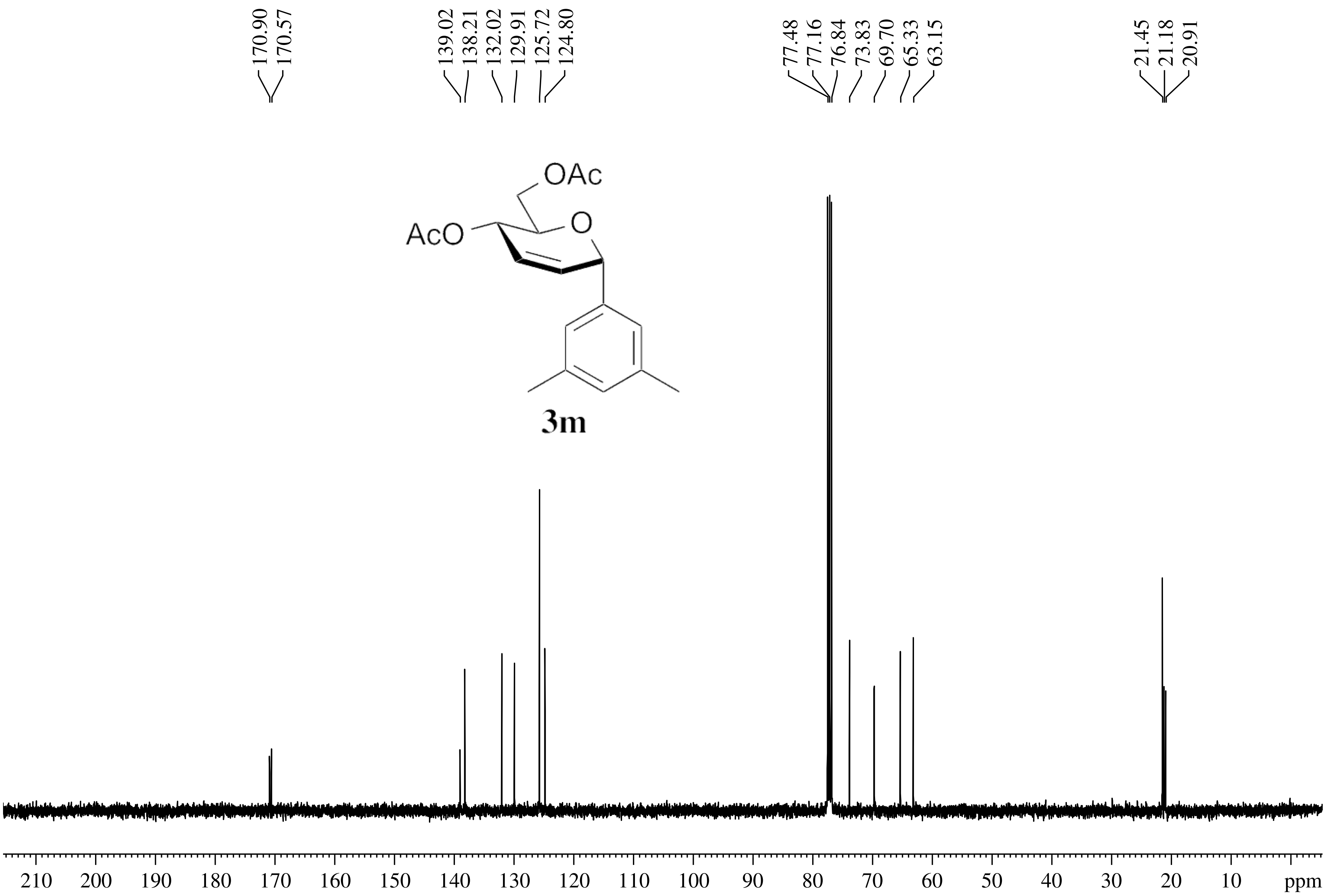
1H NMR, CDCl3, 400 MHz



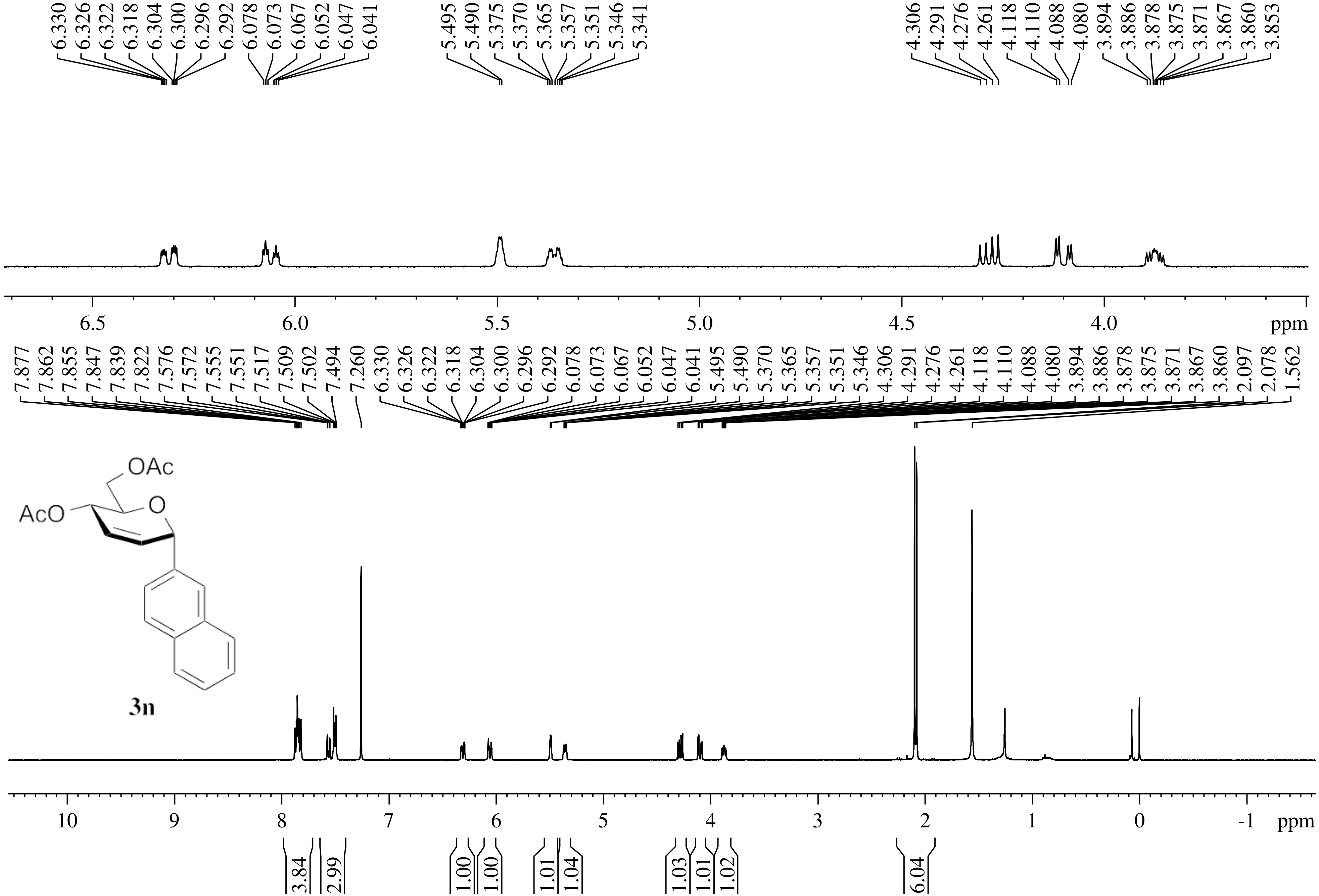
1H NMR, CDCl3, 400 MHz



1H NMR, CDCl3, 400 MHz

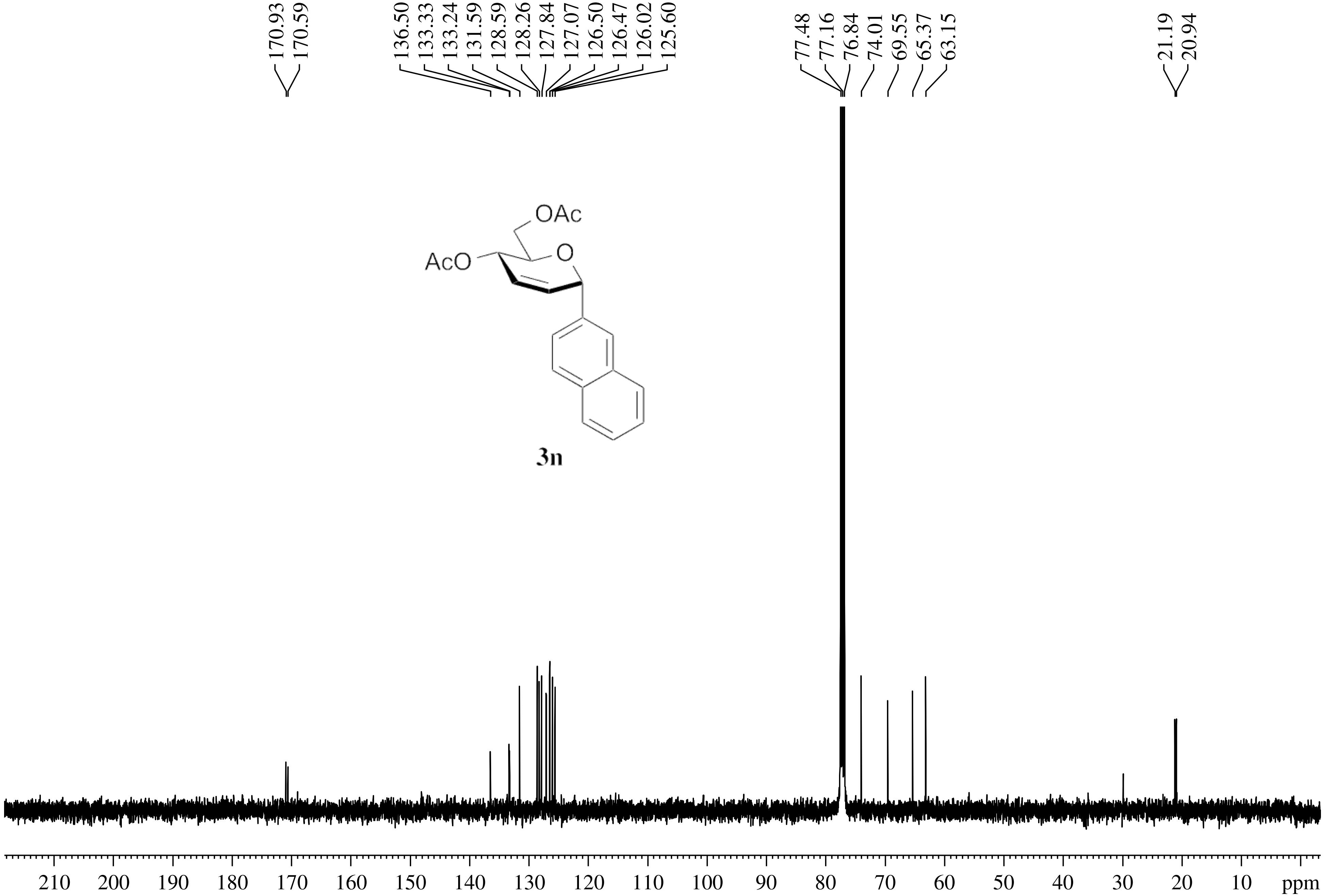


1H NMR, CDCl3, 400 MHz



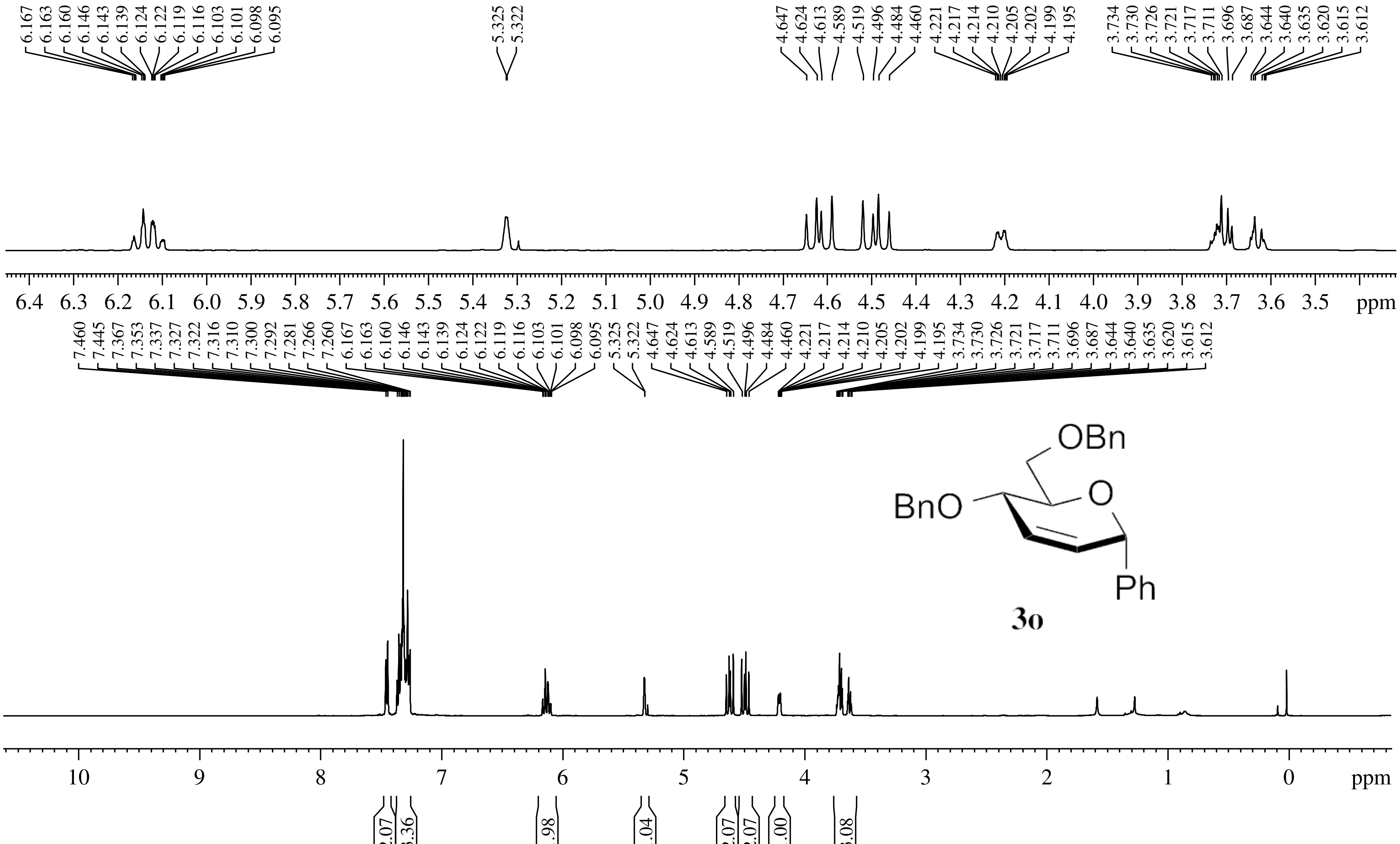
3n

1H NMR, CDCl3, 400 MHz



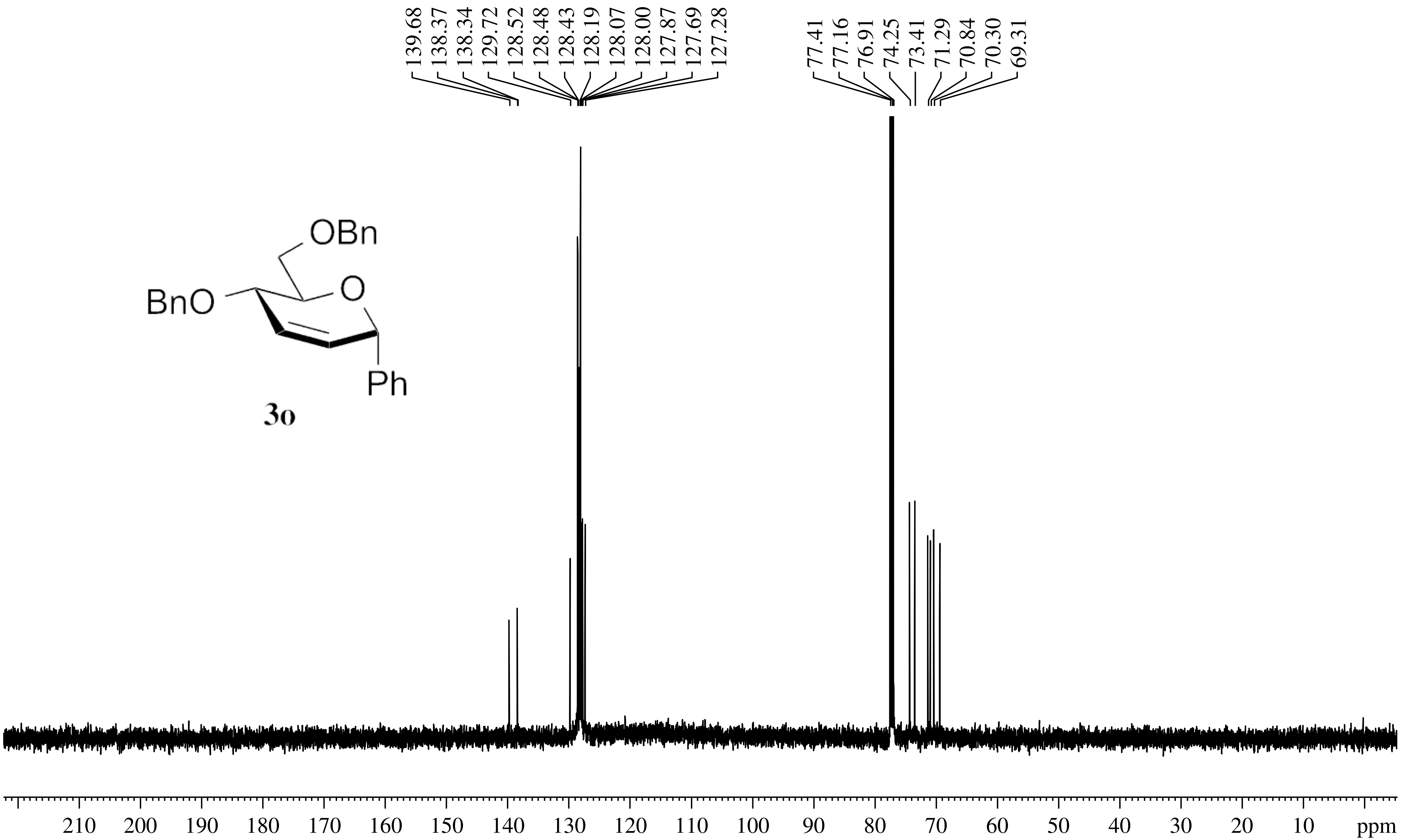
3n

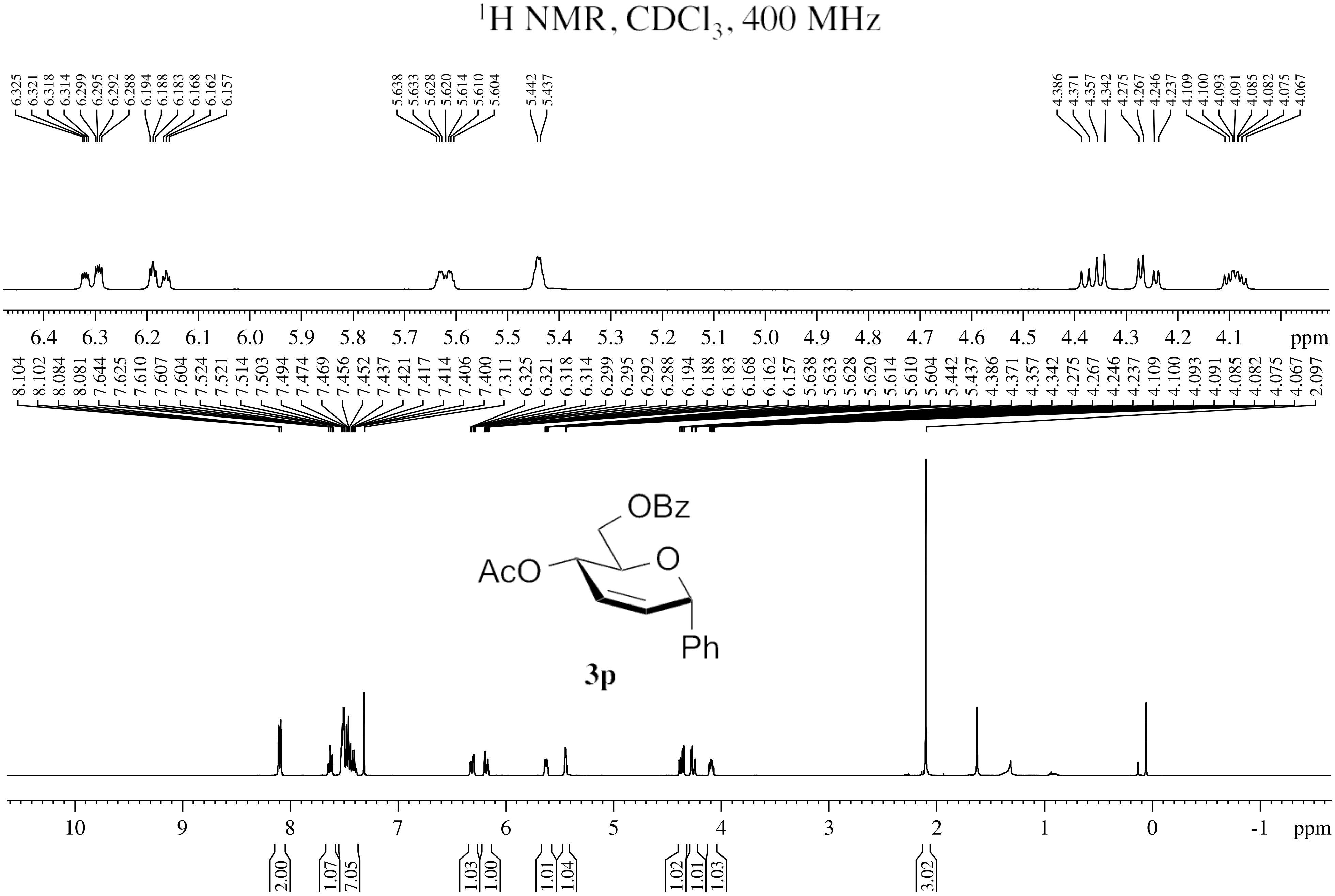
^{1}H NMR, $CDCl_3$, 500 MHz



3o

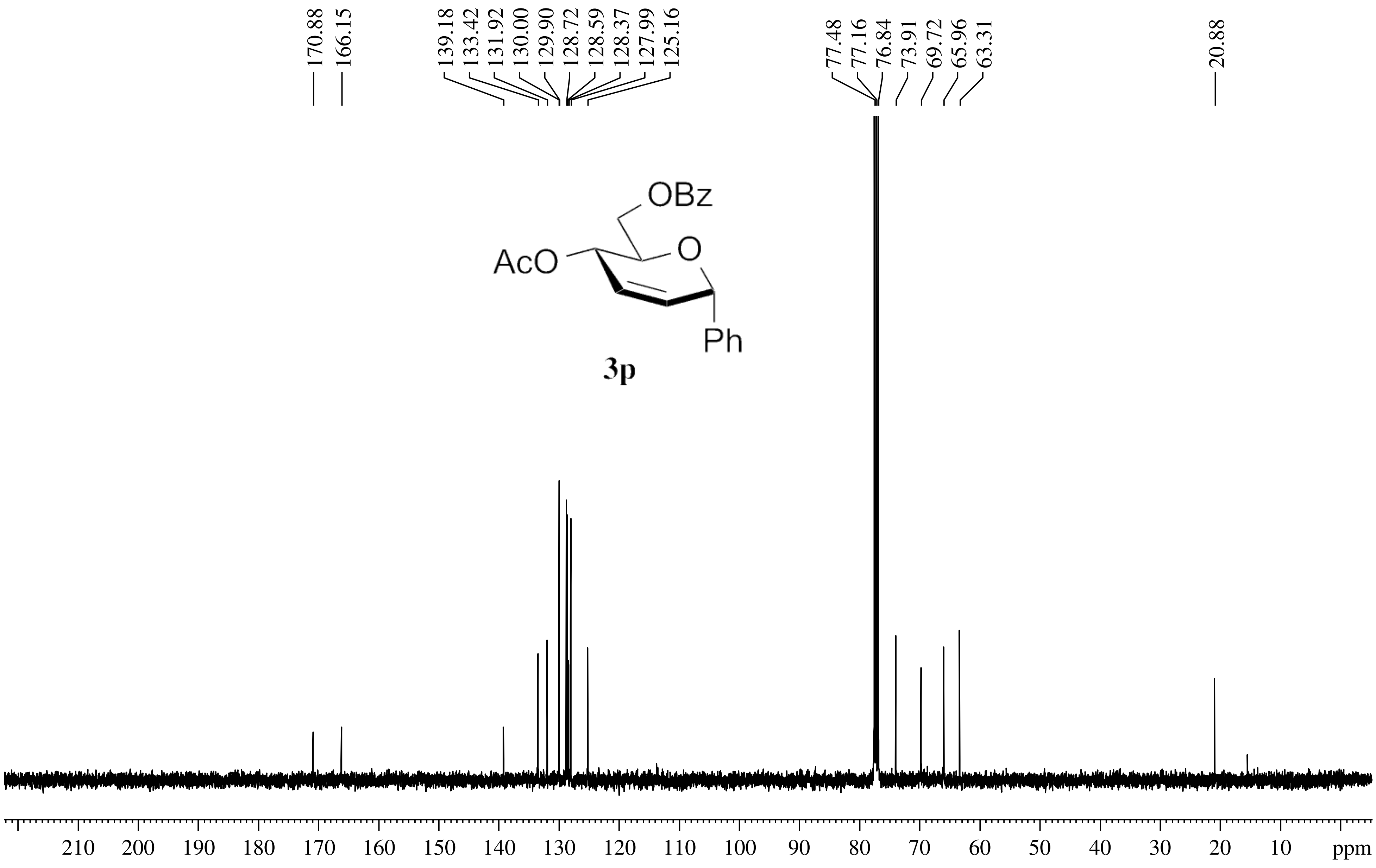
^{13}C NMR, $CDCl_3$, 125 MHz



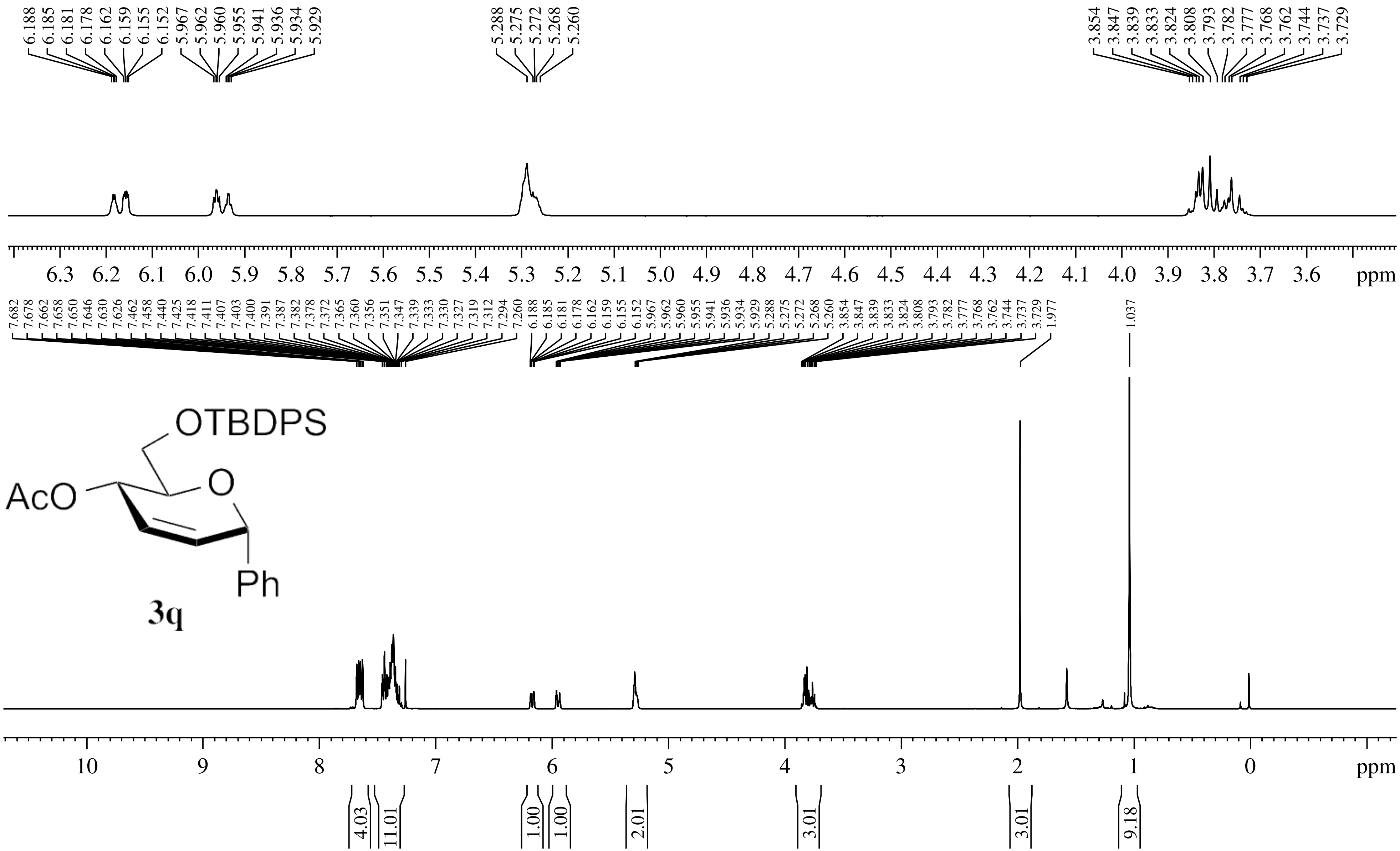


1H NMR, CDCl3, 400 MHz
OBz
AcO
O
Ph
3p
ppm

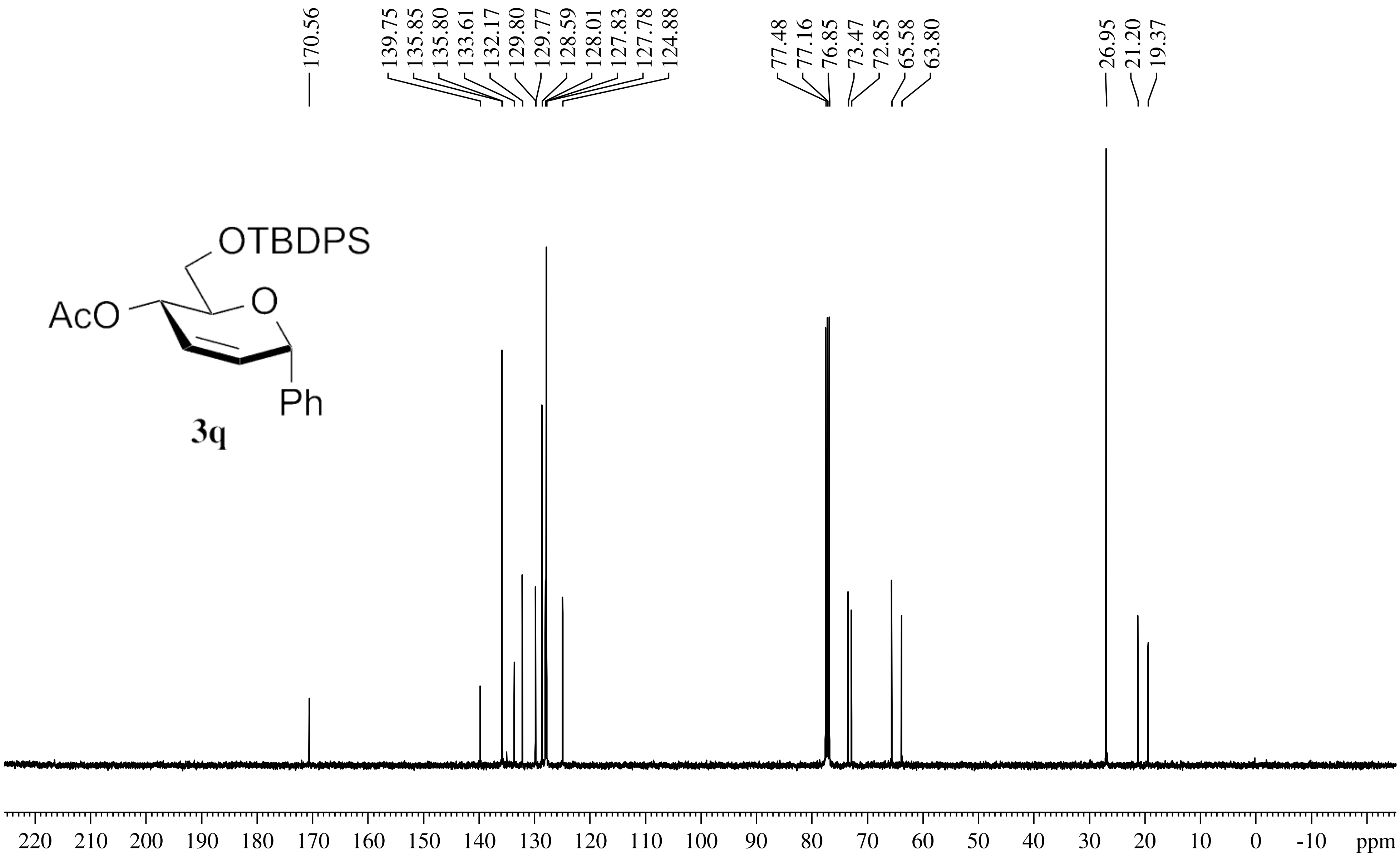
^{13}C NMR, $CDCl_3$, 100 MHz



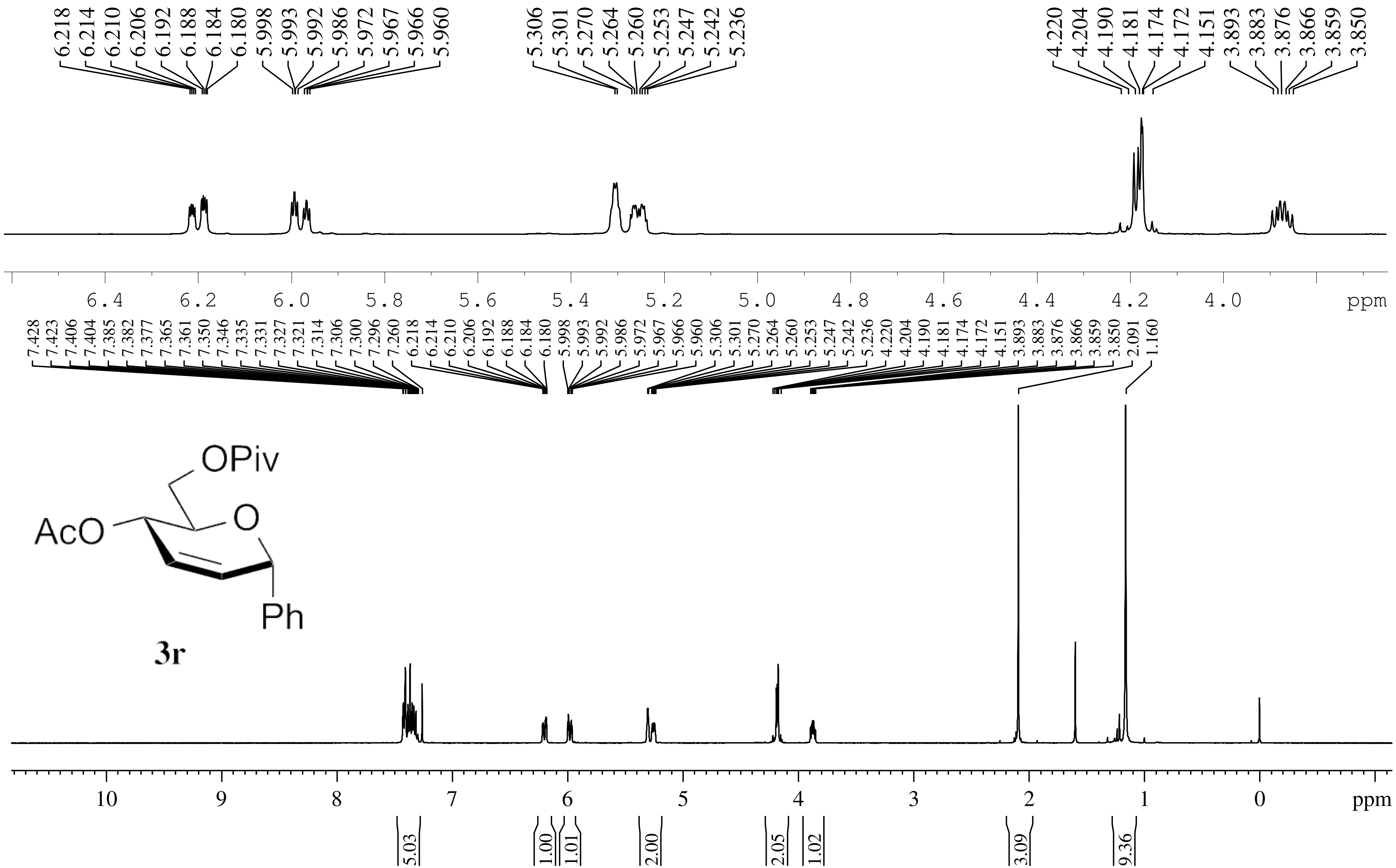
^1H NMR, $CDCl_3$, 400 MHz



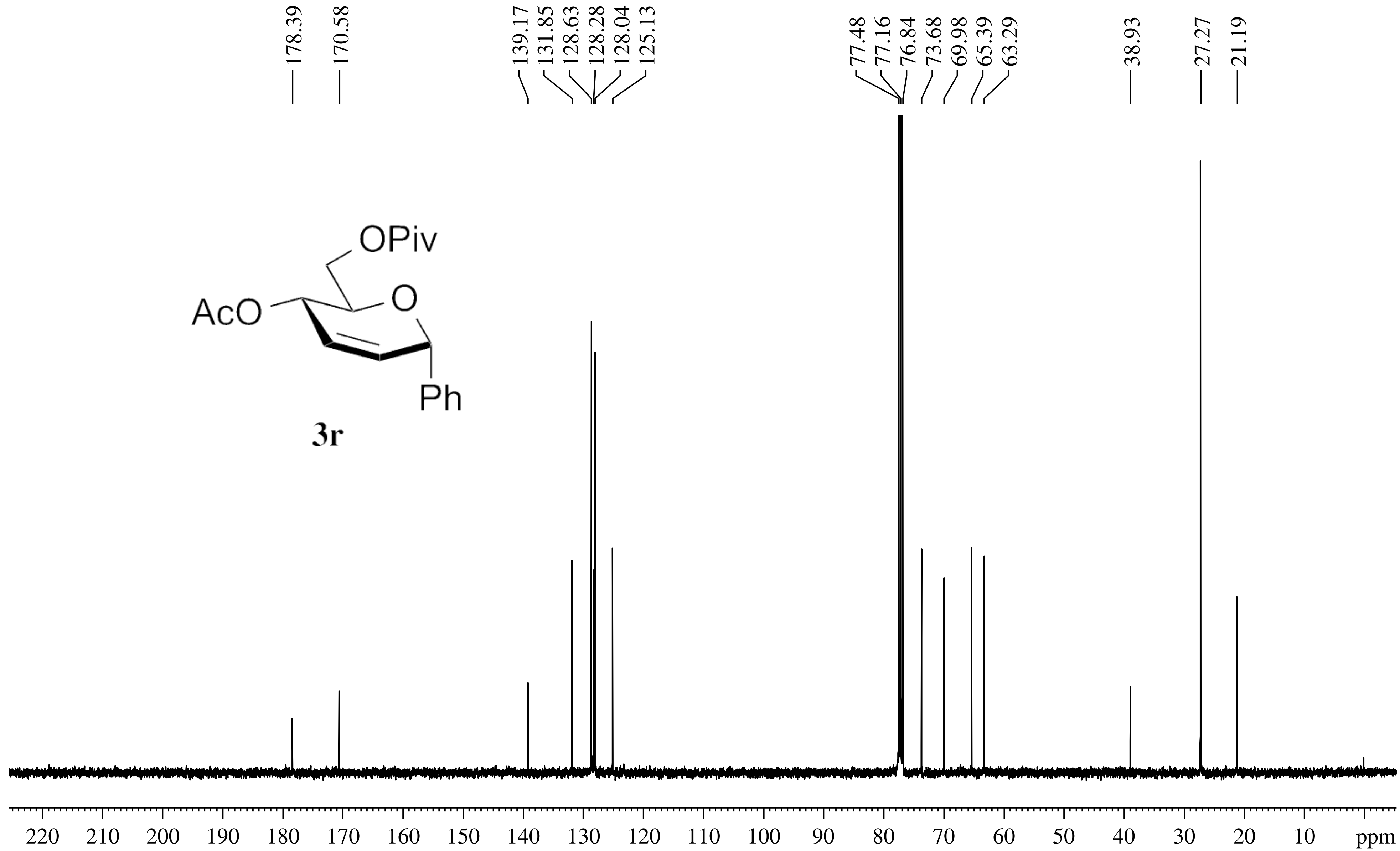
^{13}C NMR, $CDCl_3$, 100 MHz



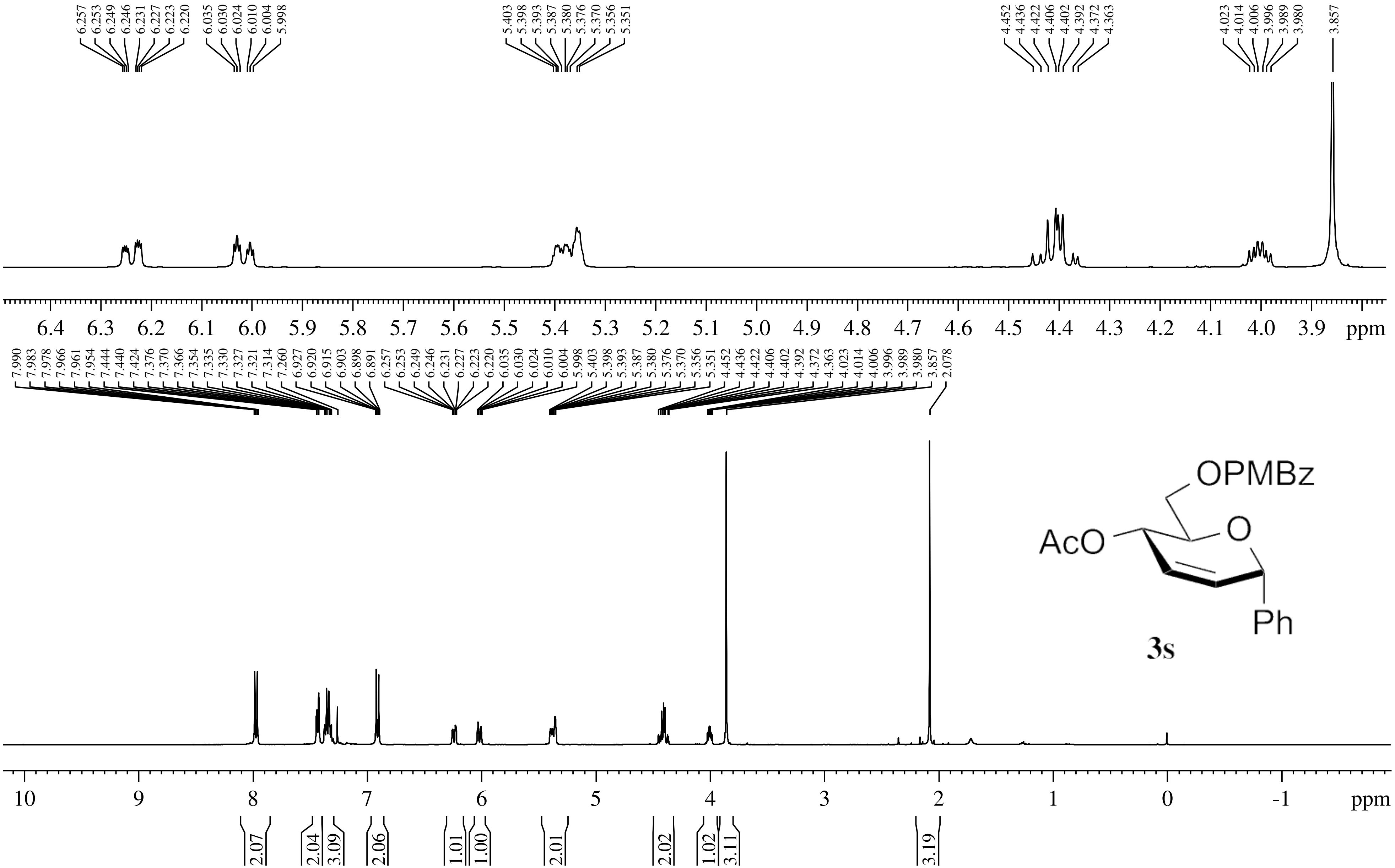
^{1}H NMR, $CDCl_3$, 400 MHz



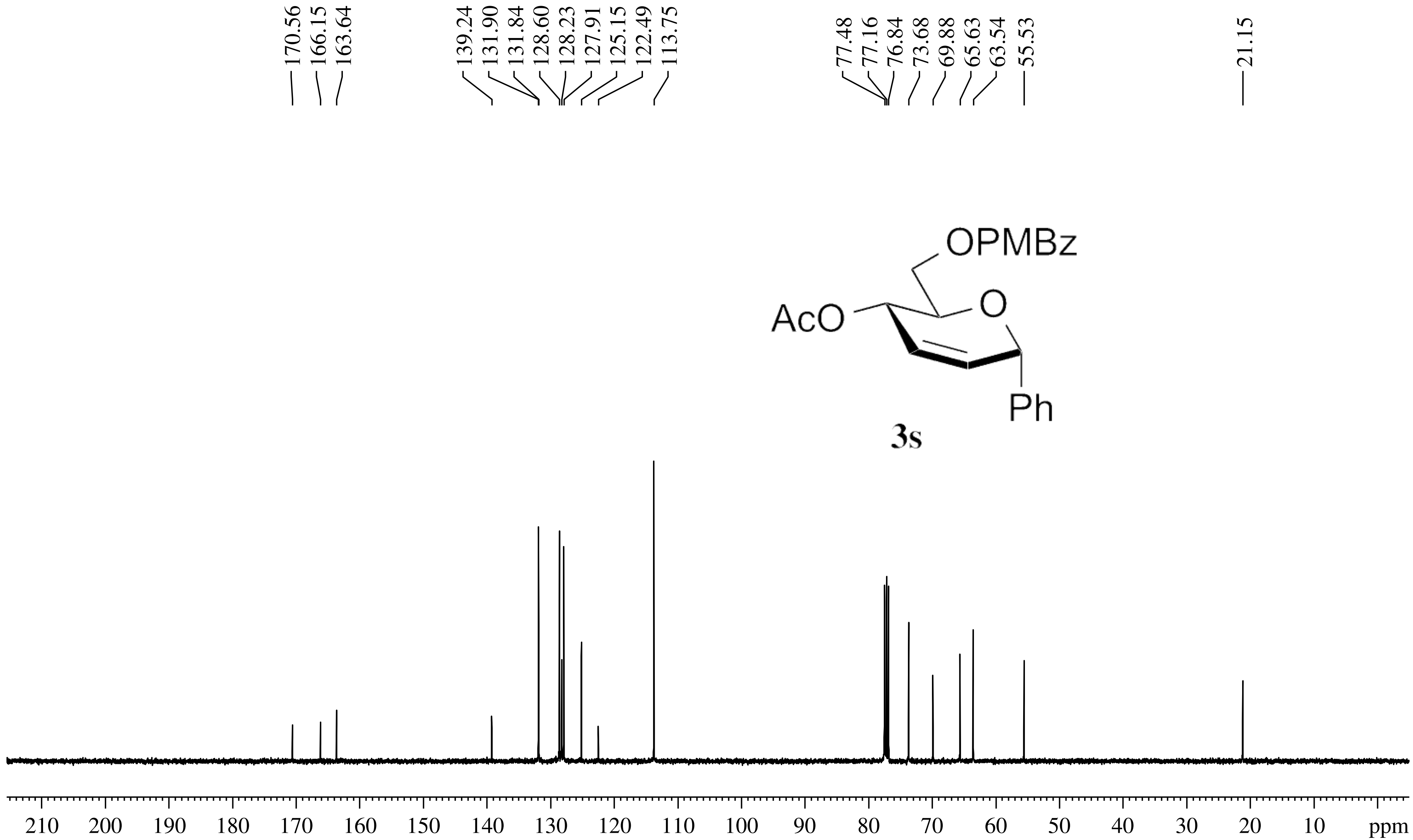
^{13}C NMR, $CDCl_3$, 100 MHz



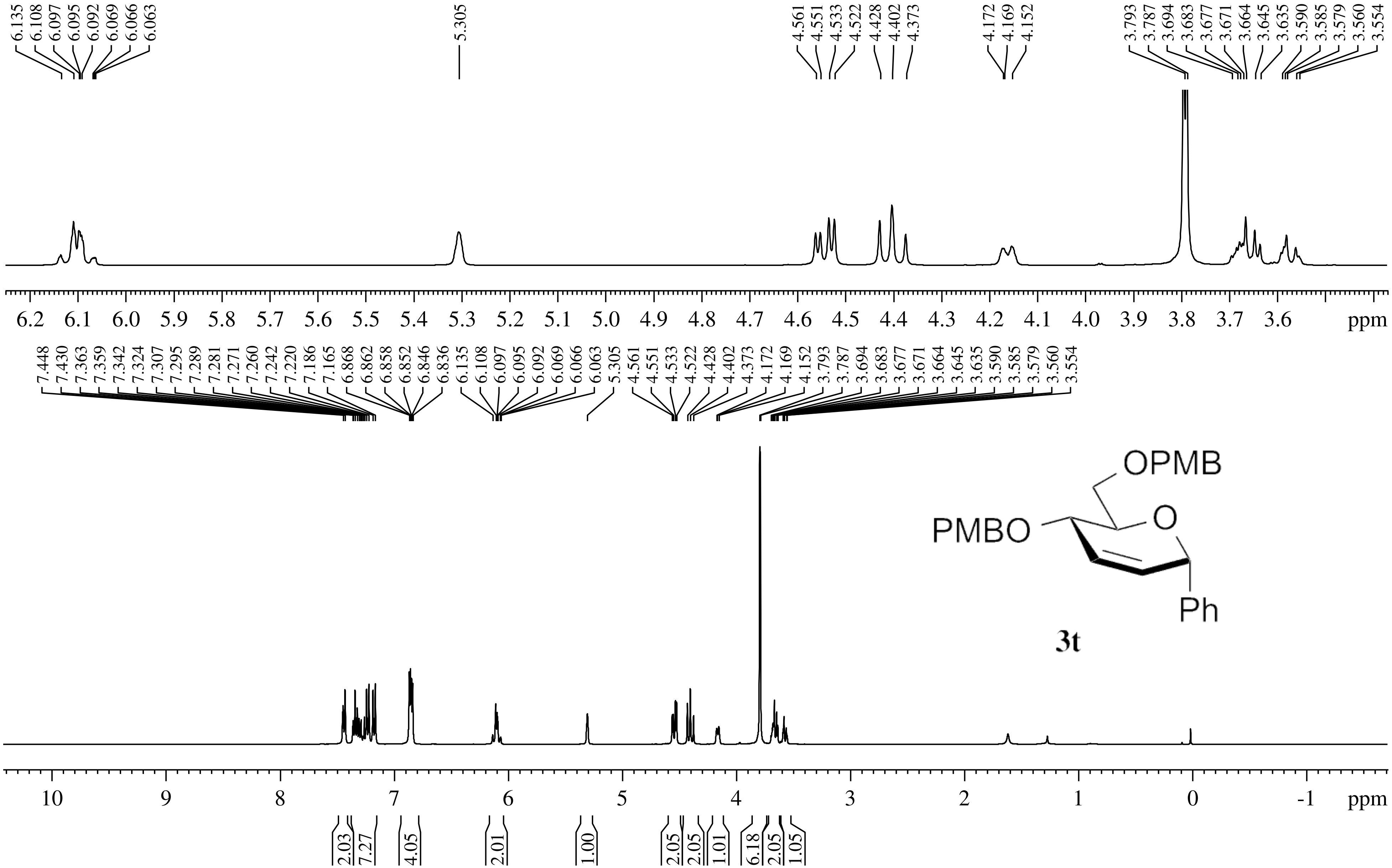
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 100 MHz

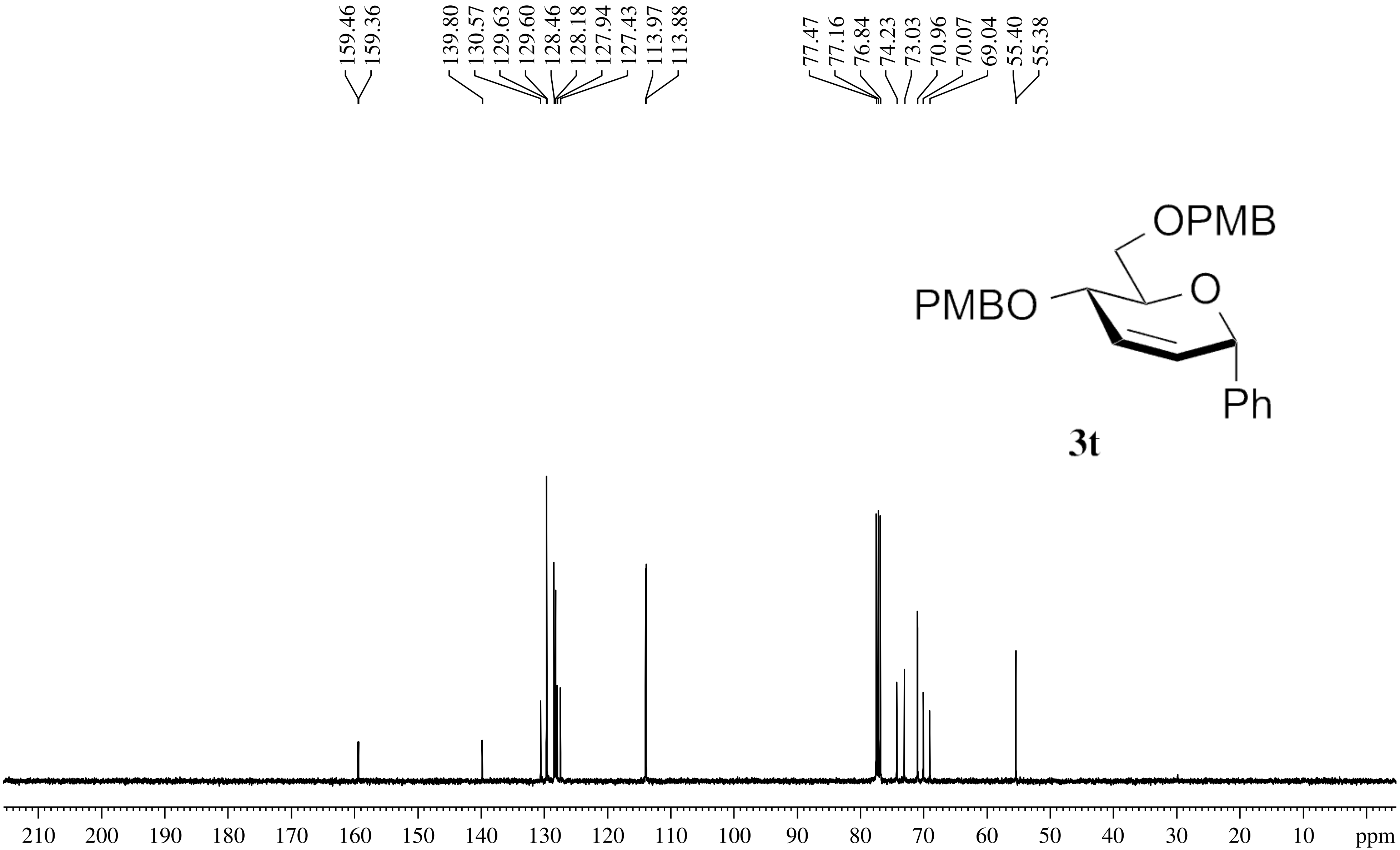


^1H NMR, $CDCl_3$, 400 MHz



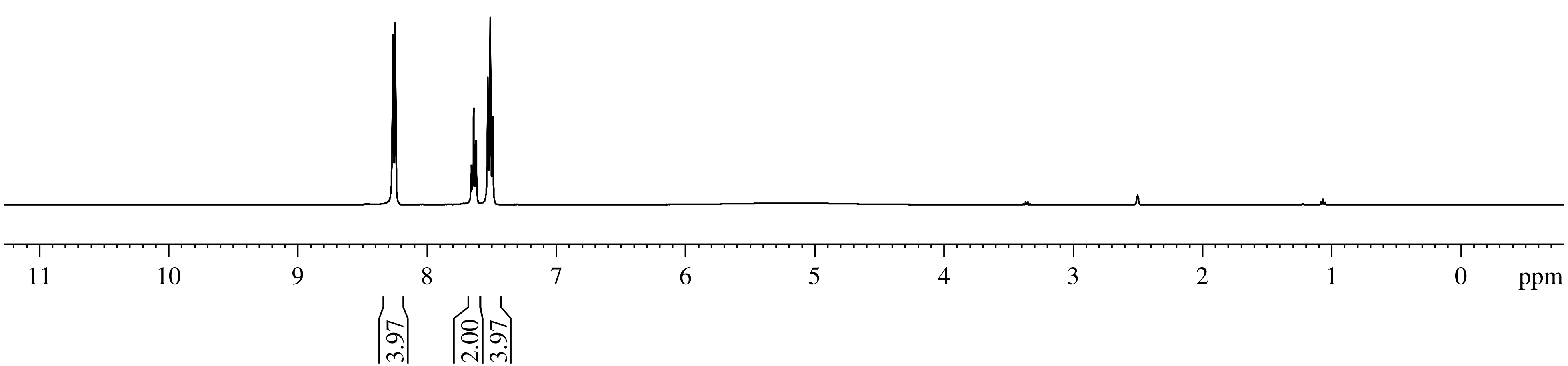
3t

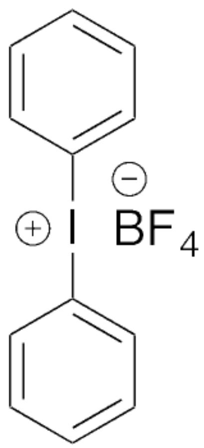
^{13}C NMR, $CDCl_3$, 100 MHz



3t

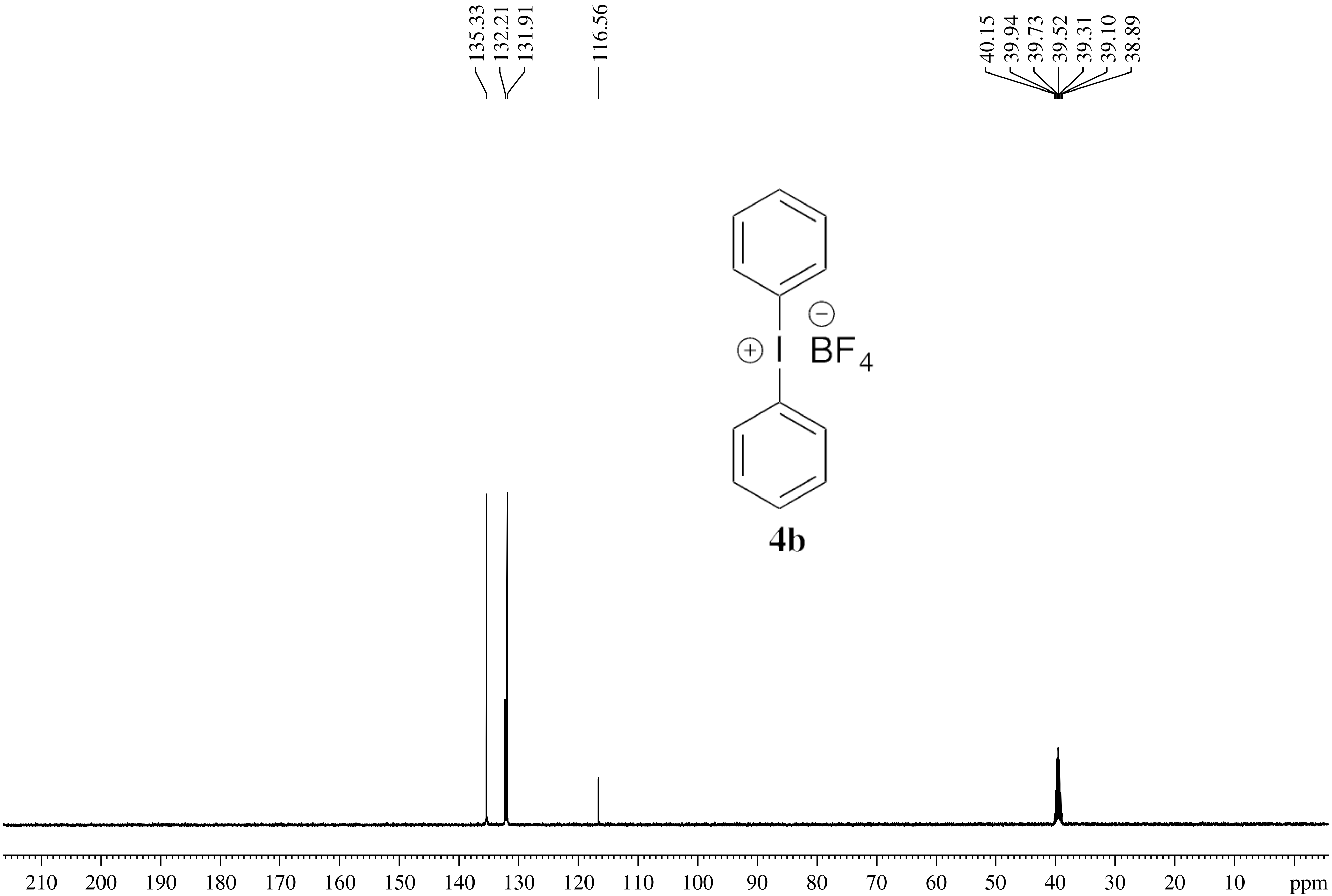
1H NMR, (CD3)2SO, 400 MHz



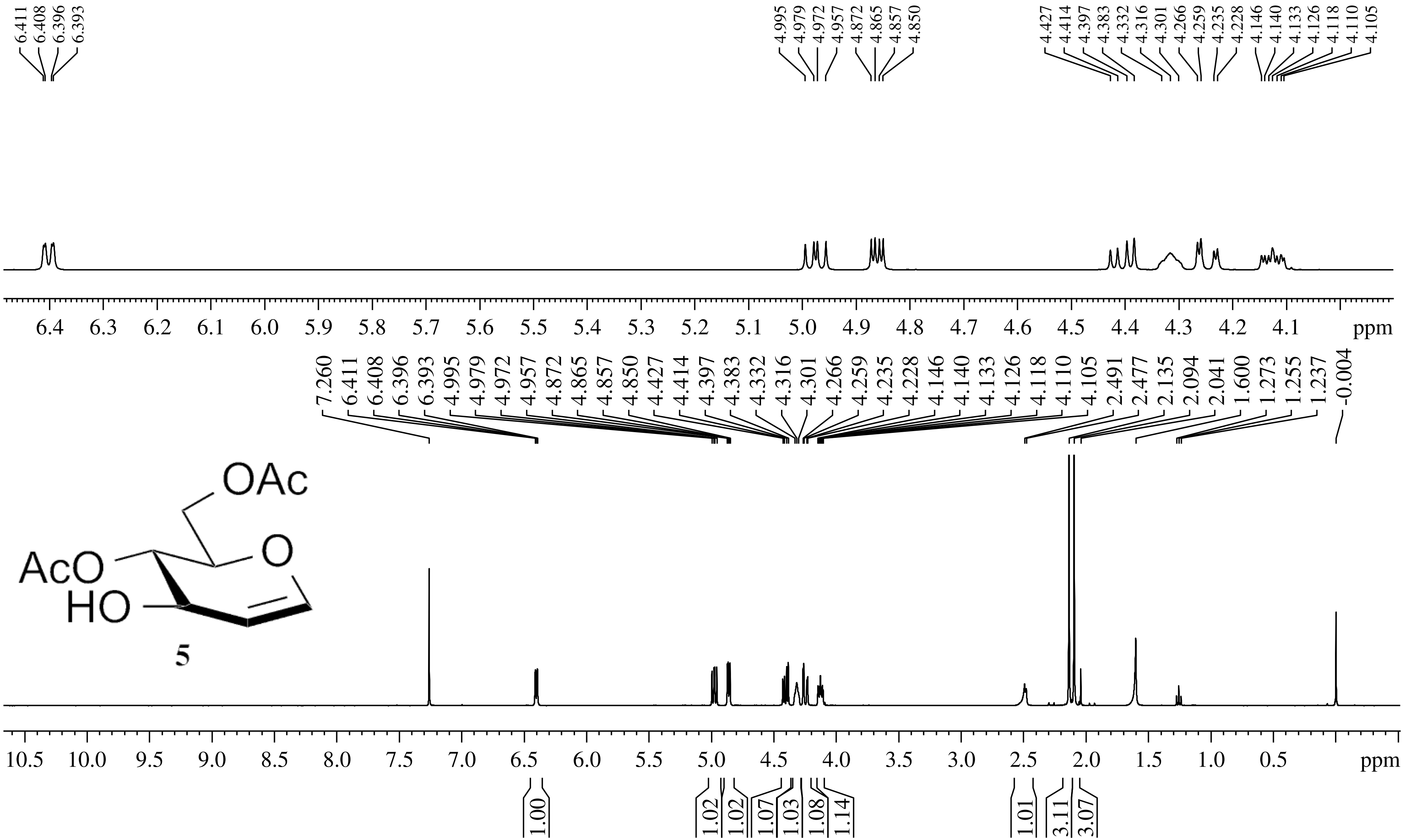


4b

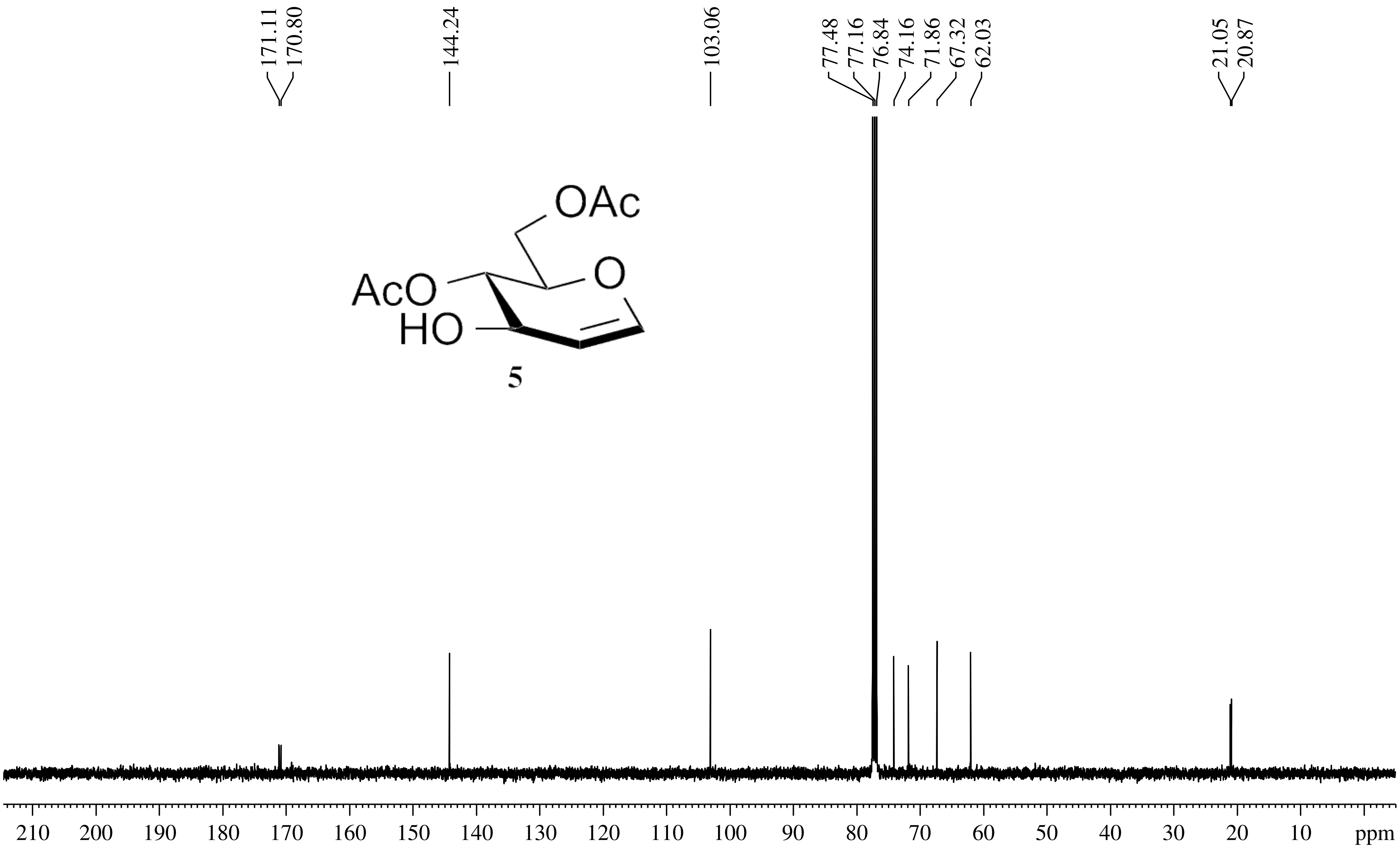
13C NMR, (CD3)2SO, 100 MHz



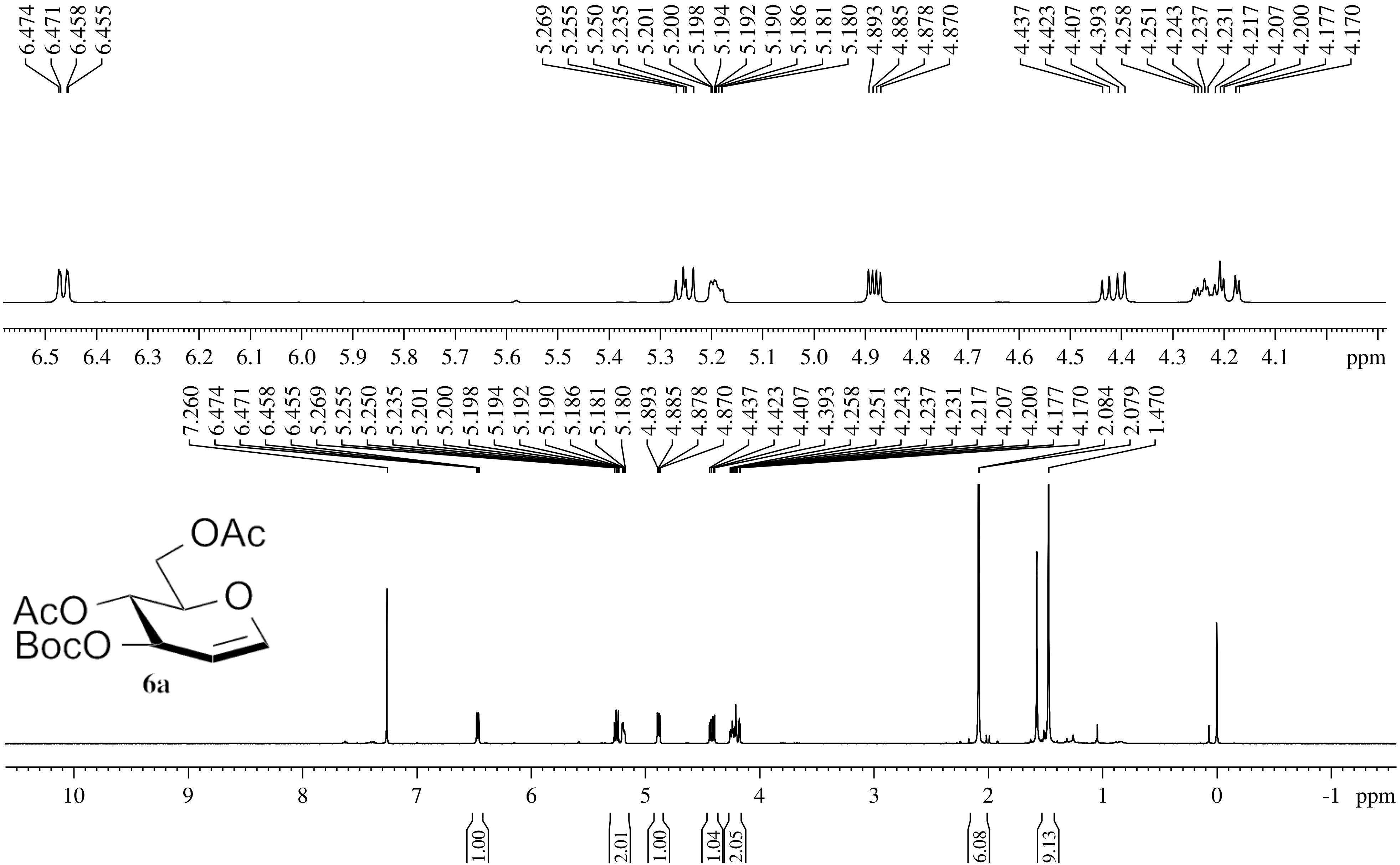
^1H NMR, $CDCl_3$, 400 MHz



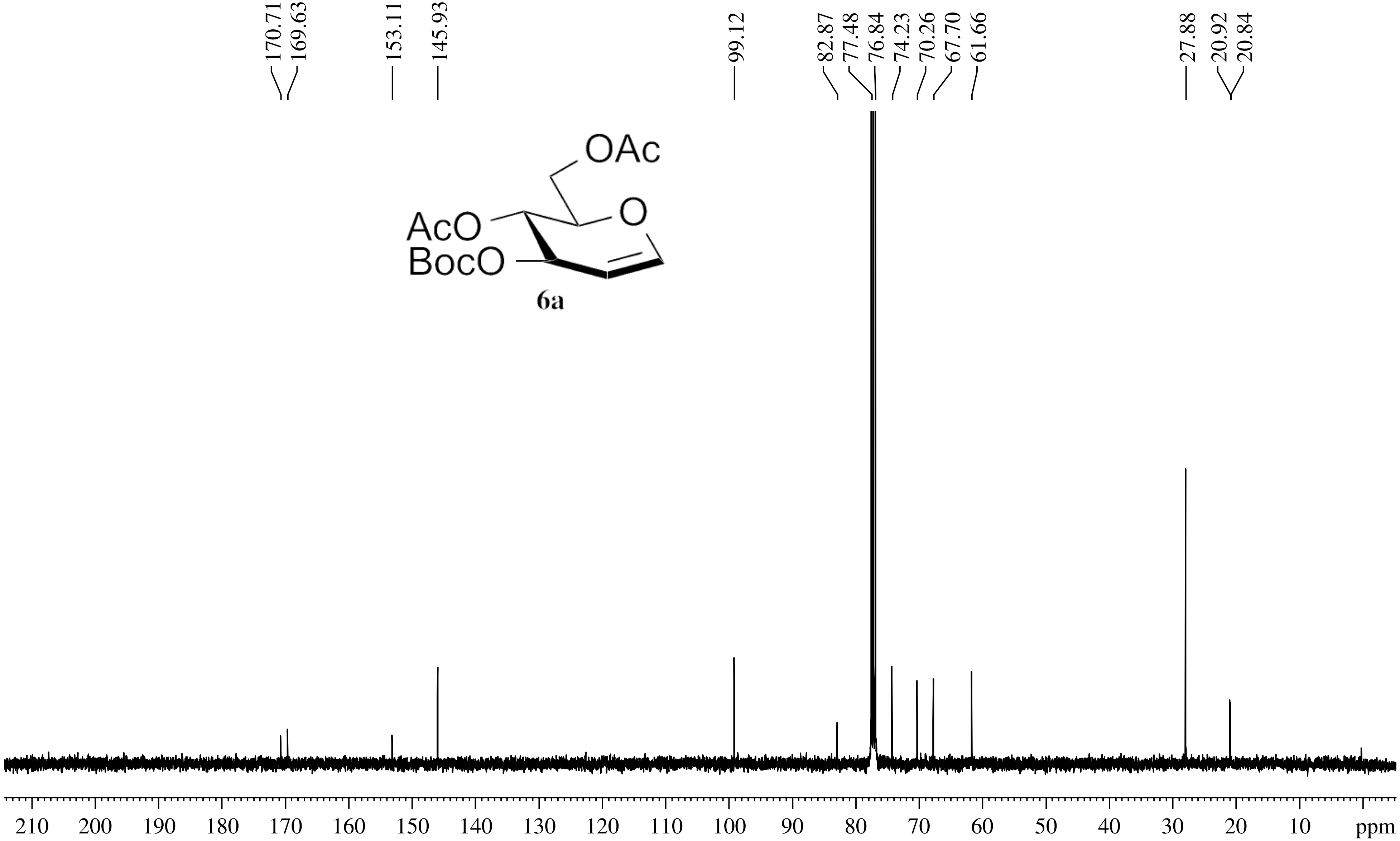
^{13}C NMR, $CDCl_3$, 100 MHz



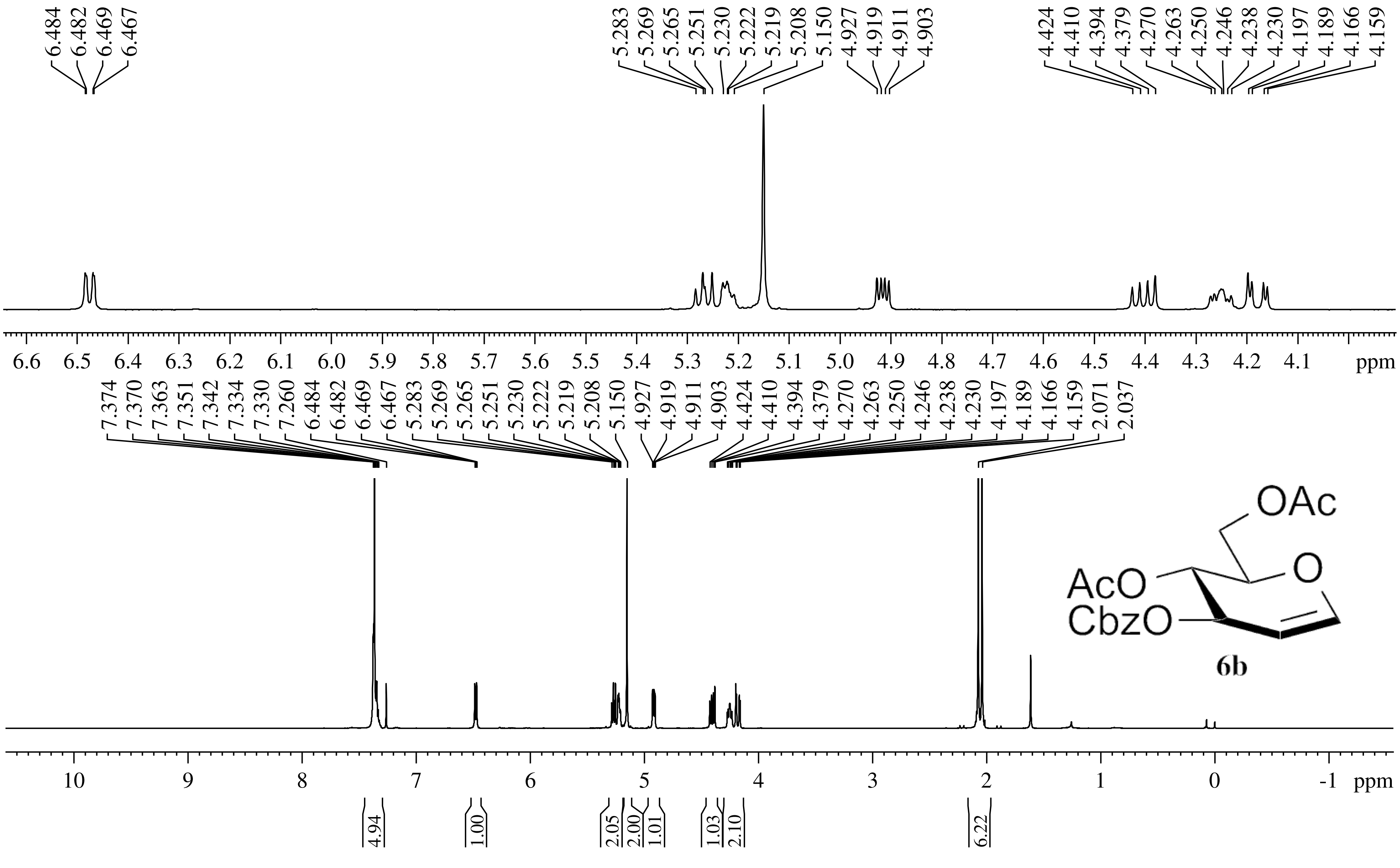
^1H NMR, $CDCl_3$, 400 MHz



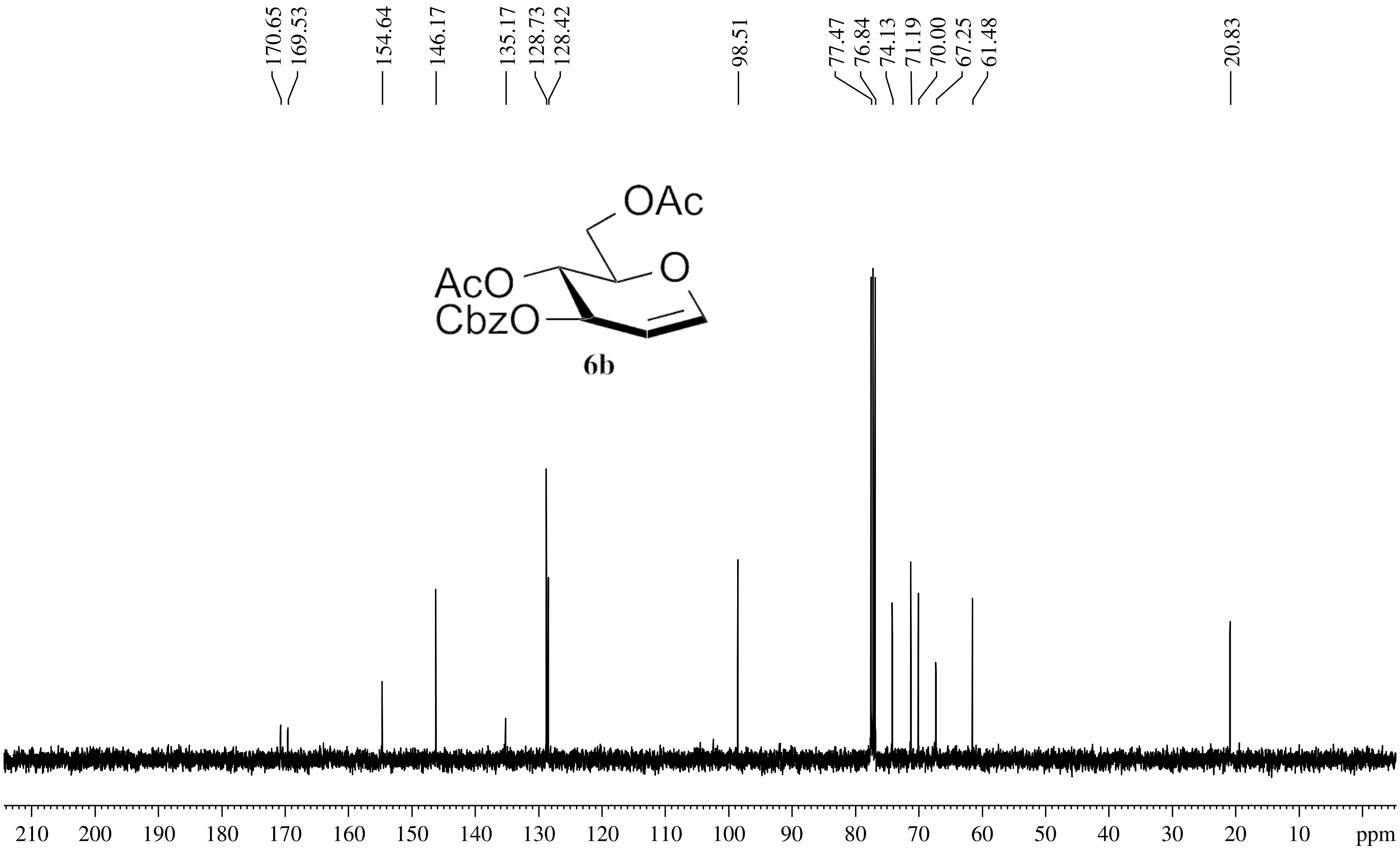
^{13}C NMR, $CDCl_3$, 100 MHz



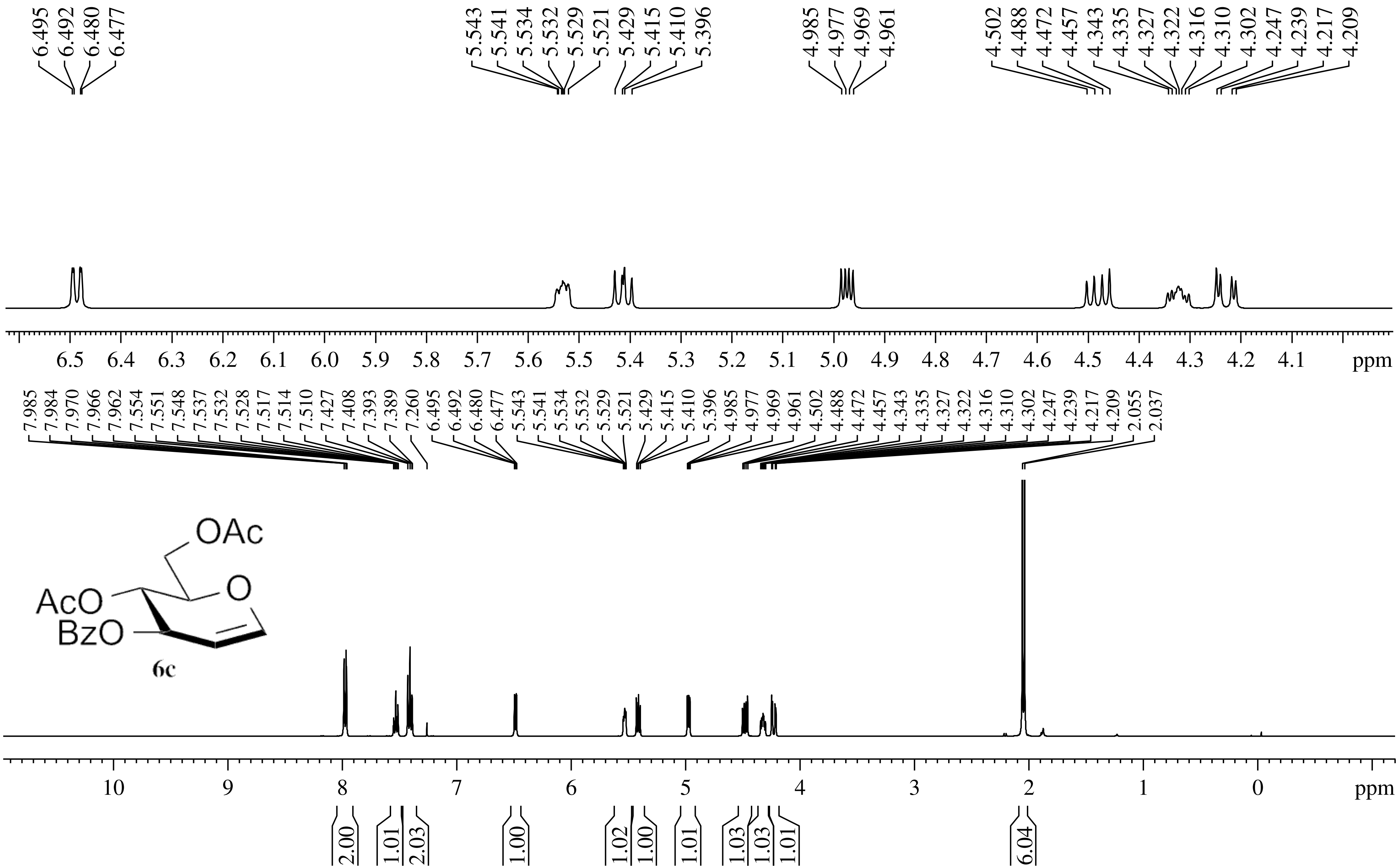
^1H NMR, $CDCl_3$, 400 MHz



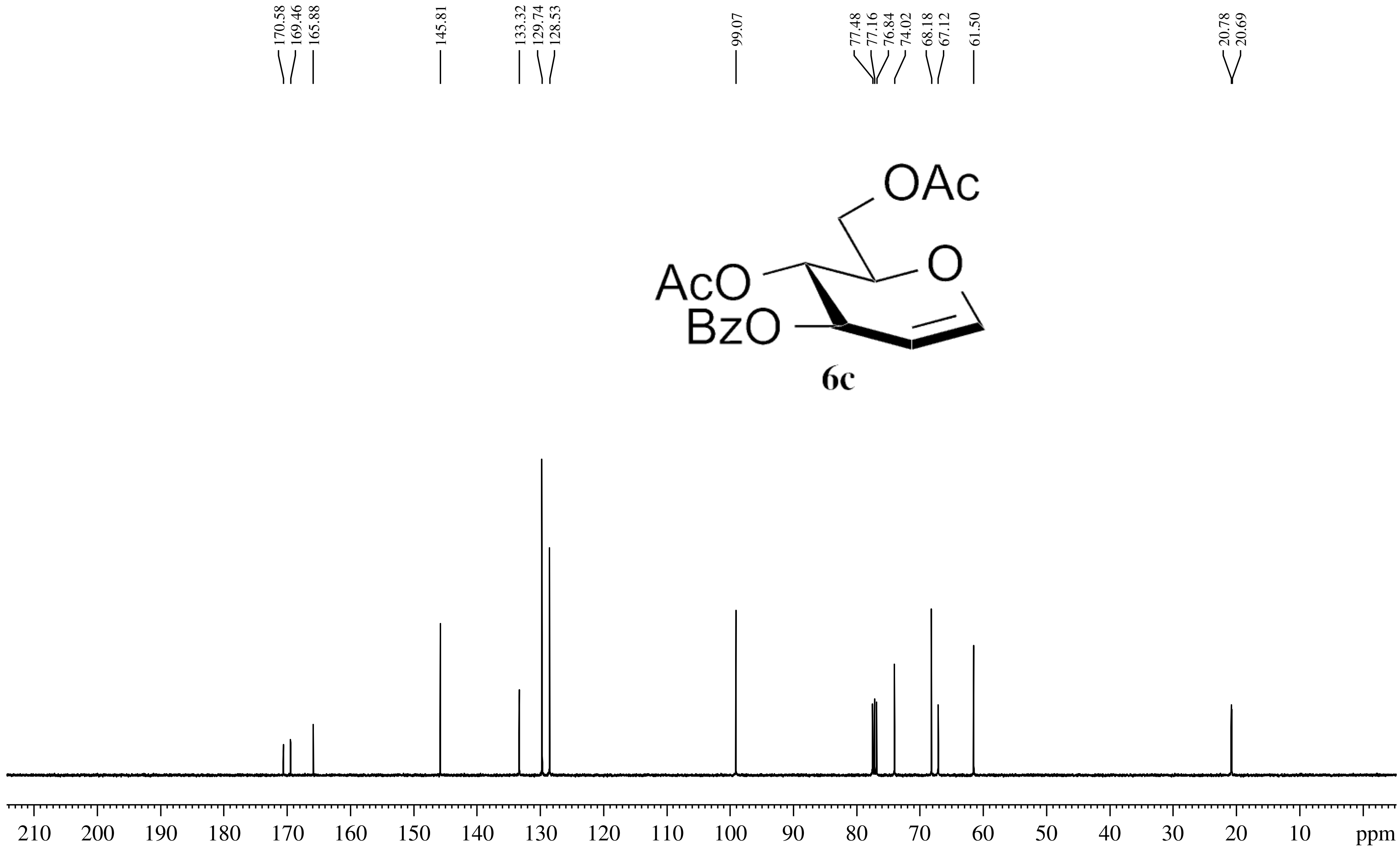
^{13}C NMR, $CDCl_3$, 100 MHz



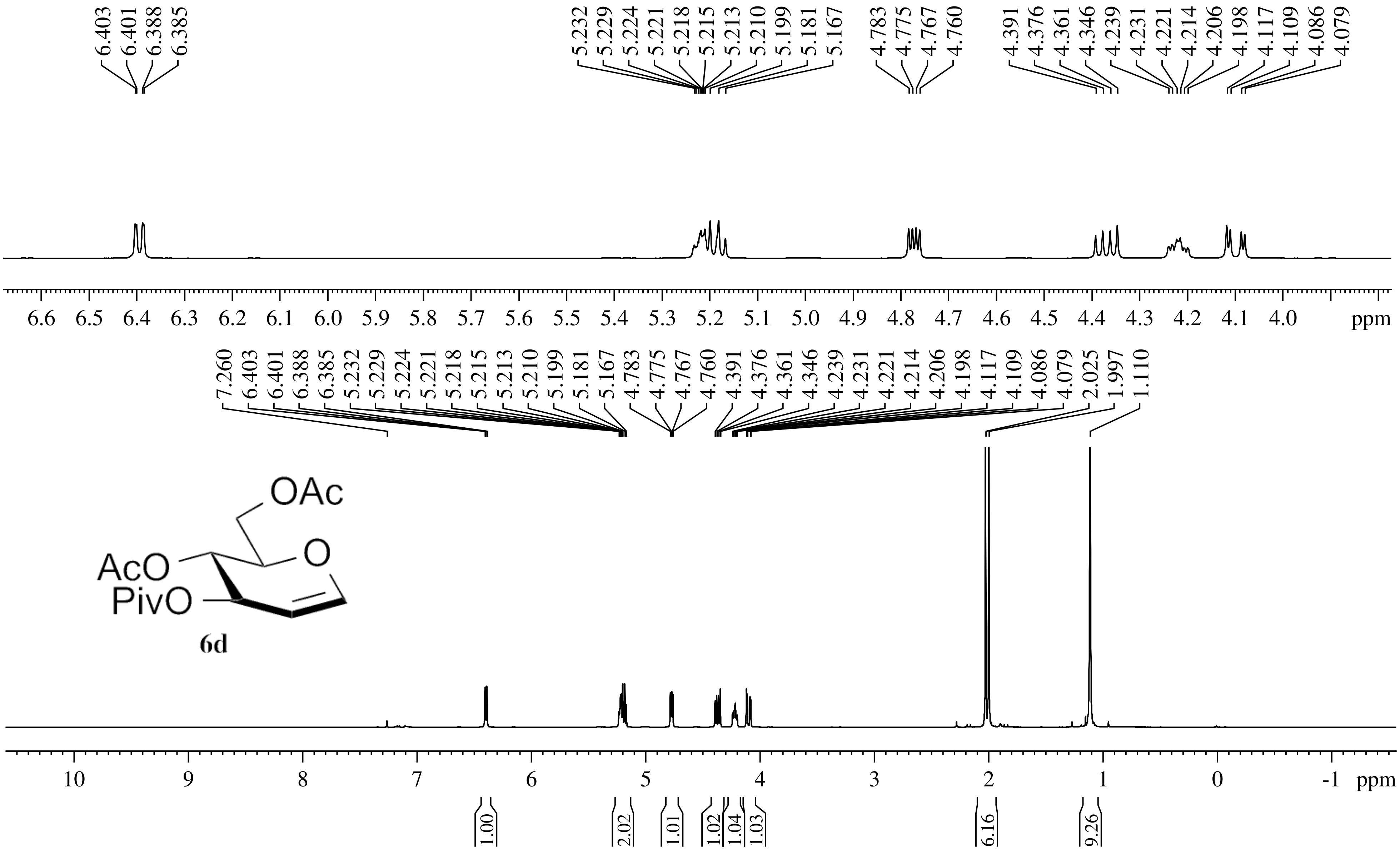
^1H NMR, $CDCl_3$, 400 MHz

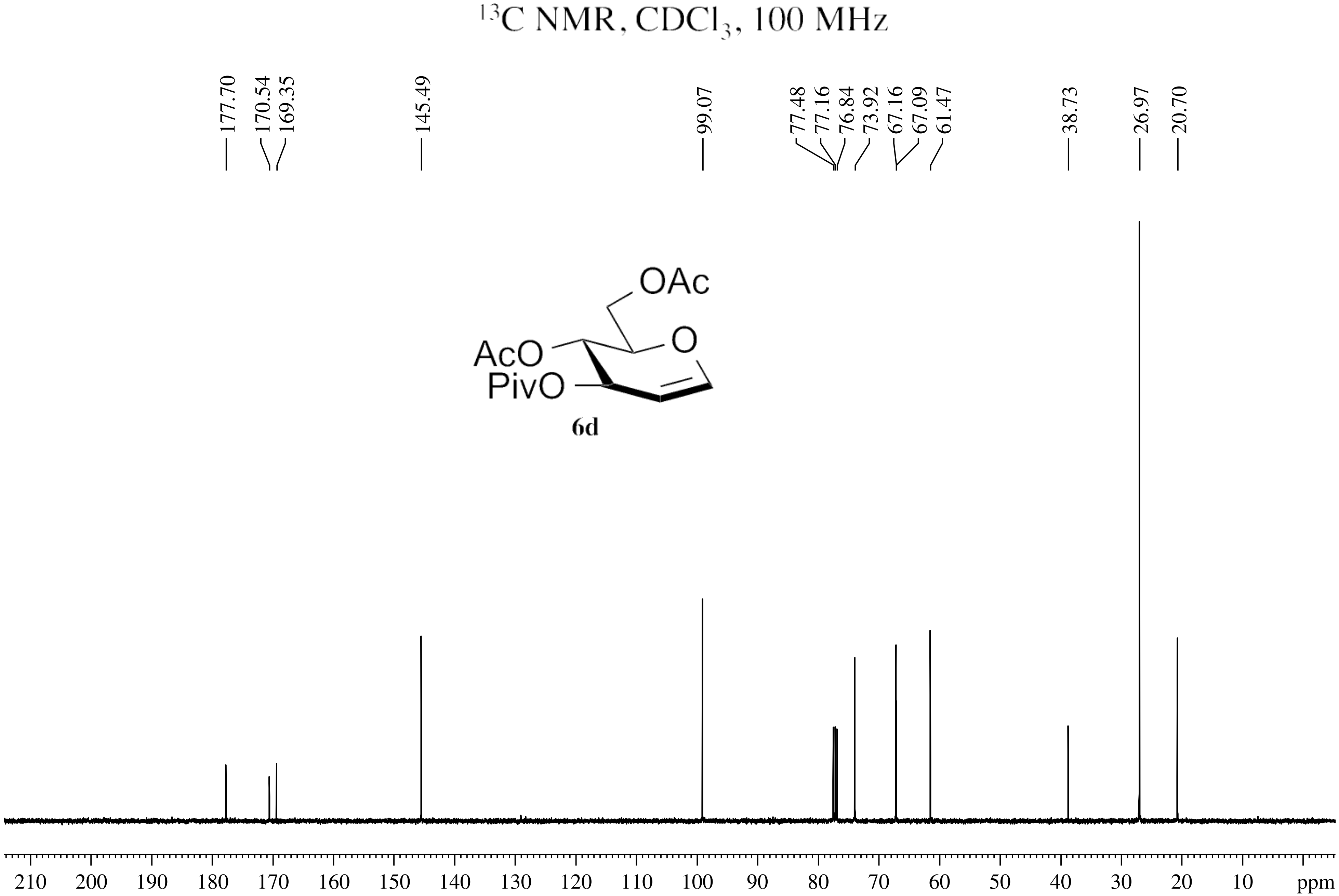


^{13}C NMR, $CDCl_3$, 100 MHz



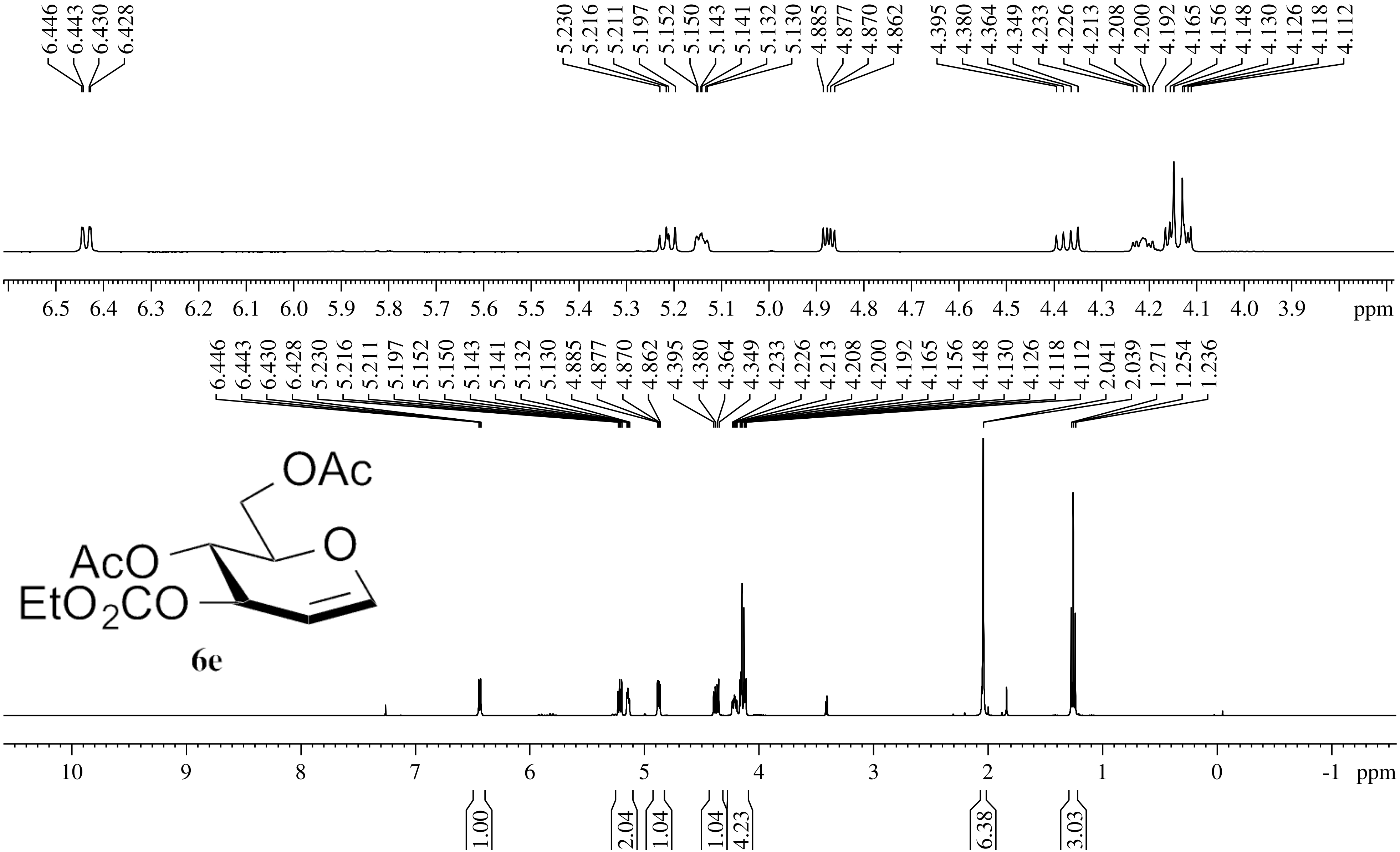
^1H NMR, $CDCl_3$, 400 MHz

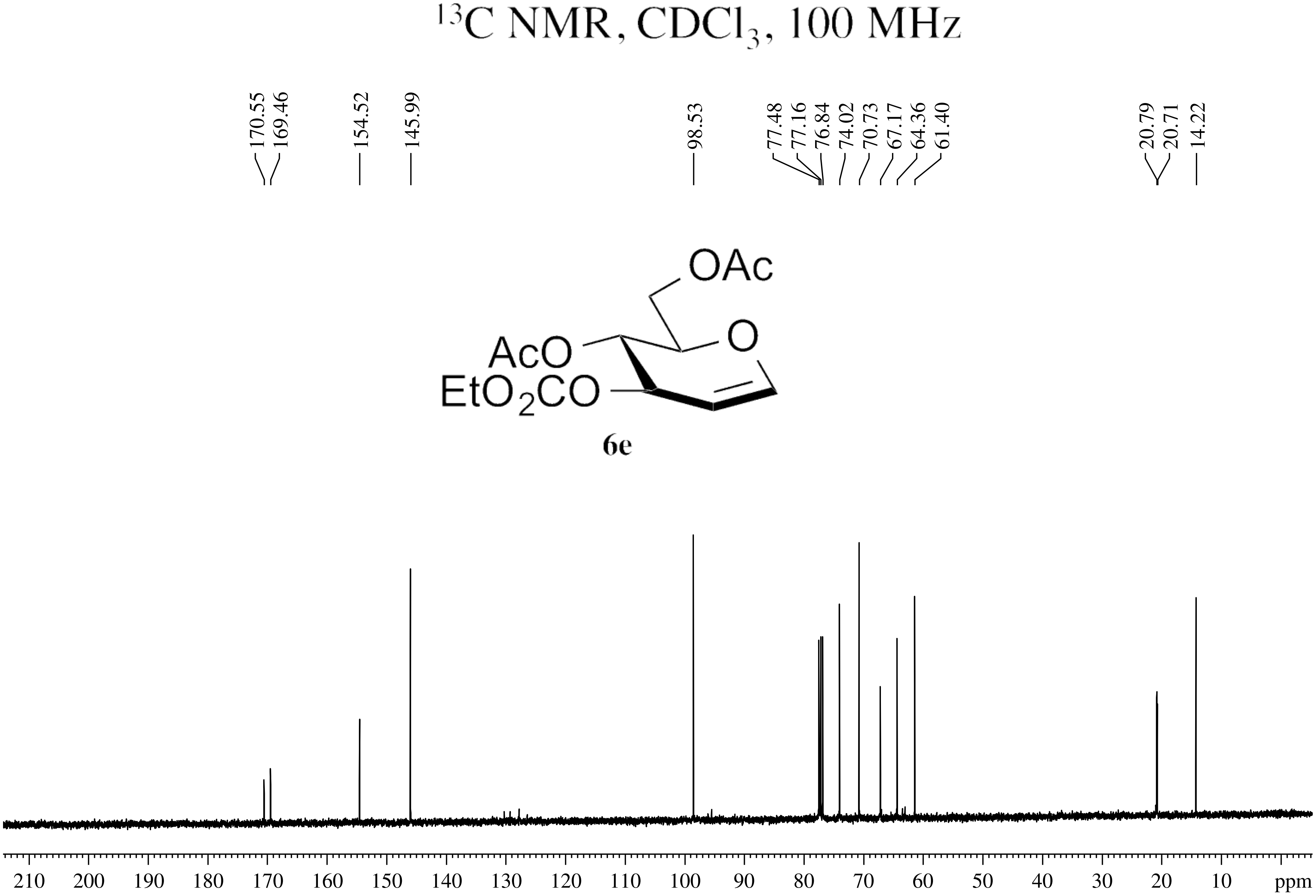




13C NMR, CDCl3, 100 MHz
177.70
170.54
169.35
145.49
99.07
77.48
77.16
76.84
73.92
67.16
67.09
61.47
38.73
26.97
20.70
OAc
AcO
PivO
O
6d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

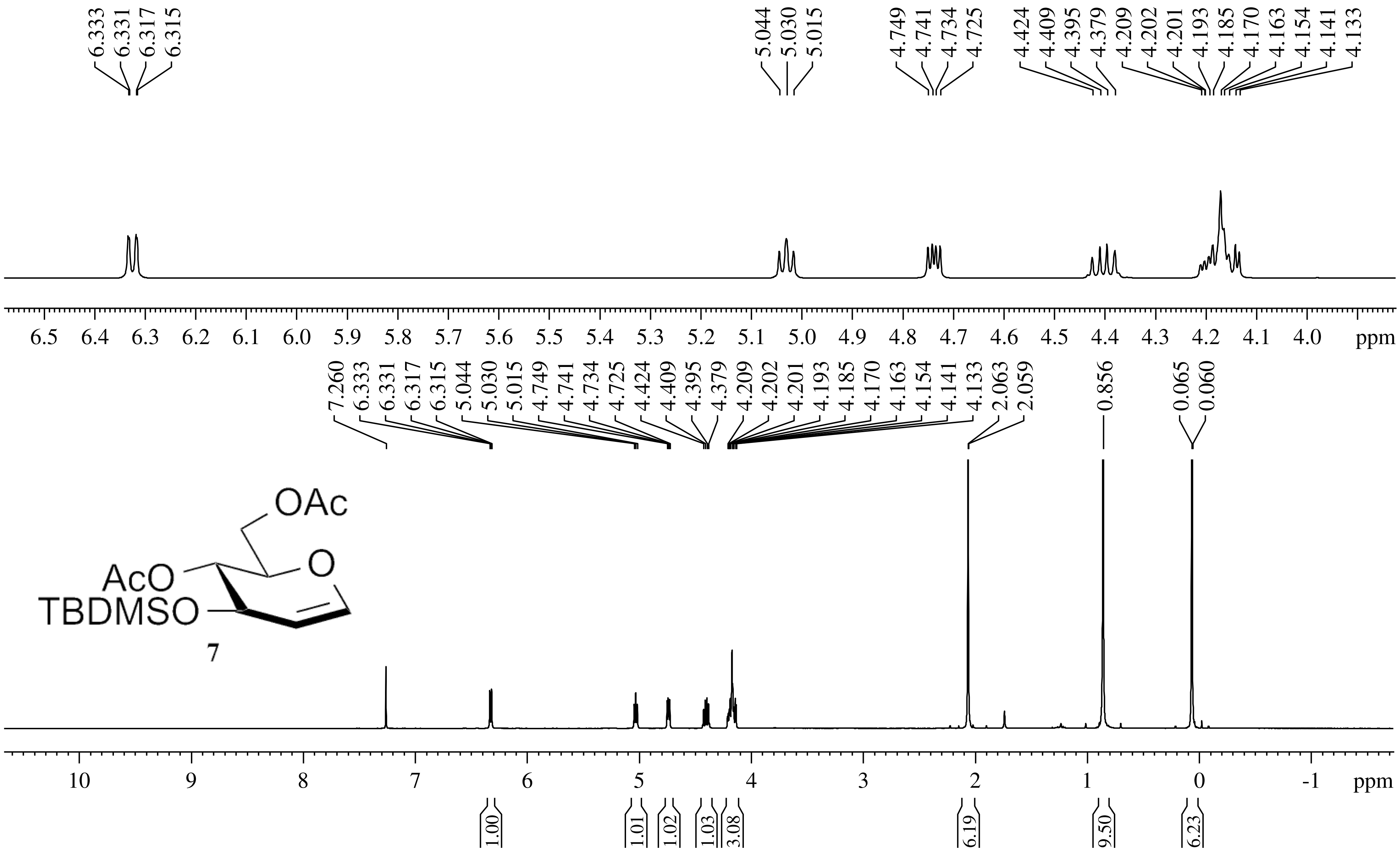
^1H NMR, $CDCl_3$, 400 MHz





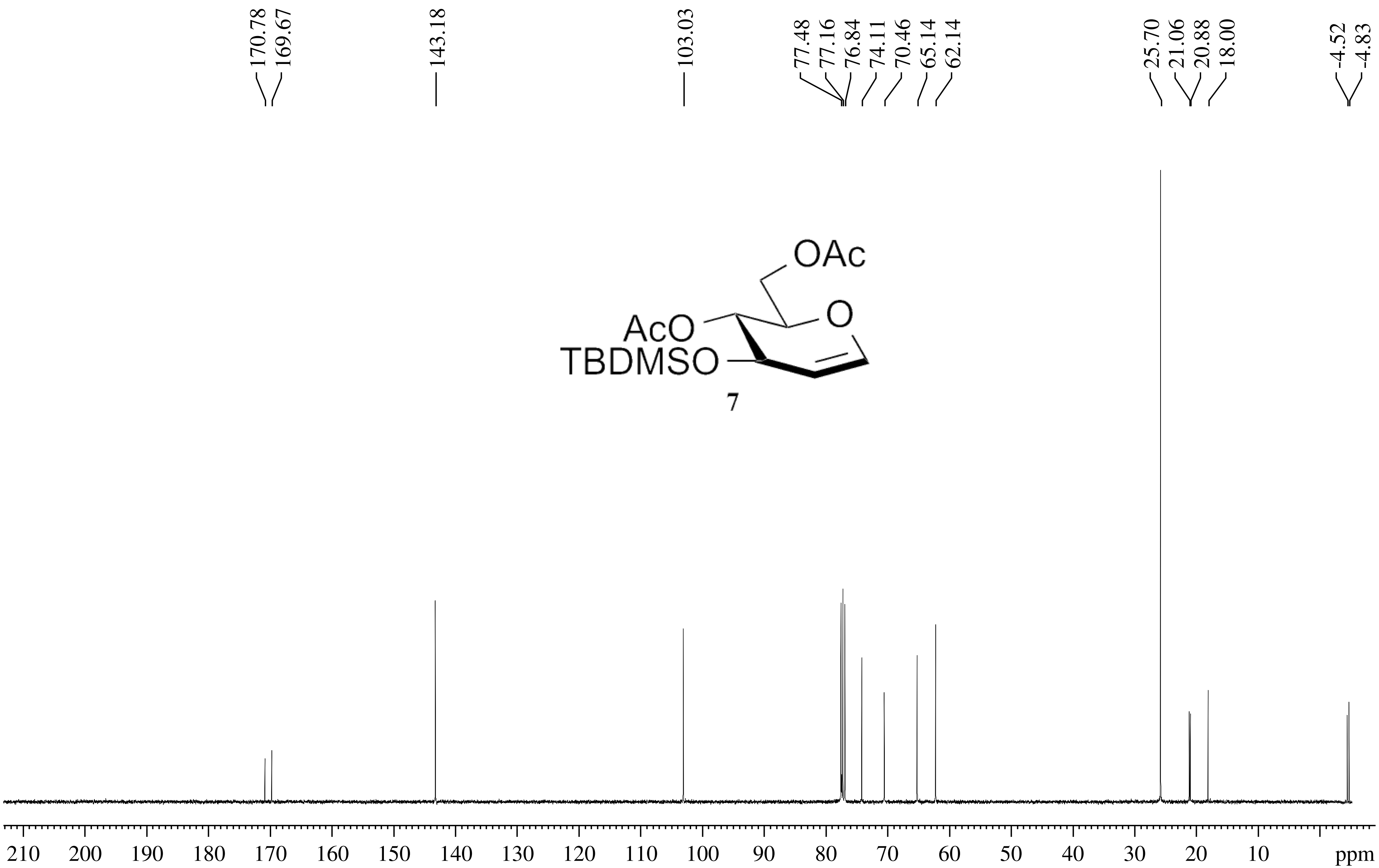
13C NMR, CDCl3, 100 MHz
170.55
169.46
154.52
145.99
98.53
77.48
77.16
76.84
74.02
70.73
67.17
64.36
61.40
20.79
20.71
14.22
OAc
O
AcO
EtO2CO
6e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H NMR, $CDCl_3$, 400 MHz

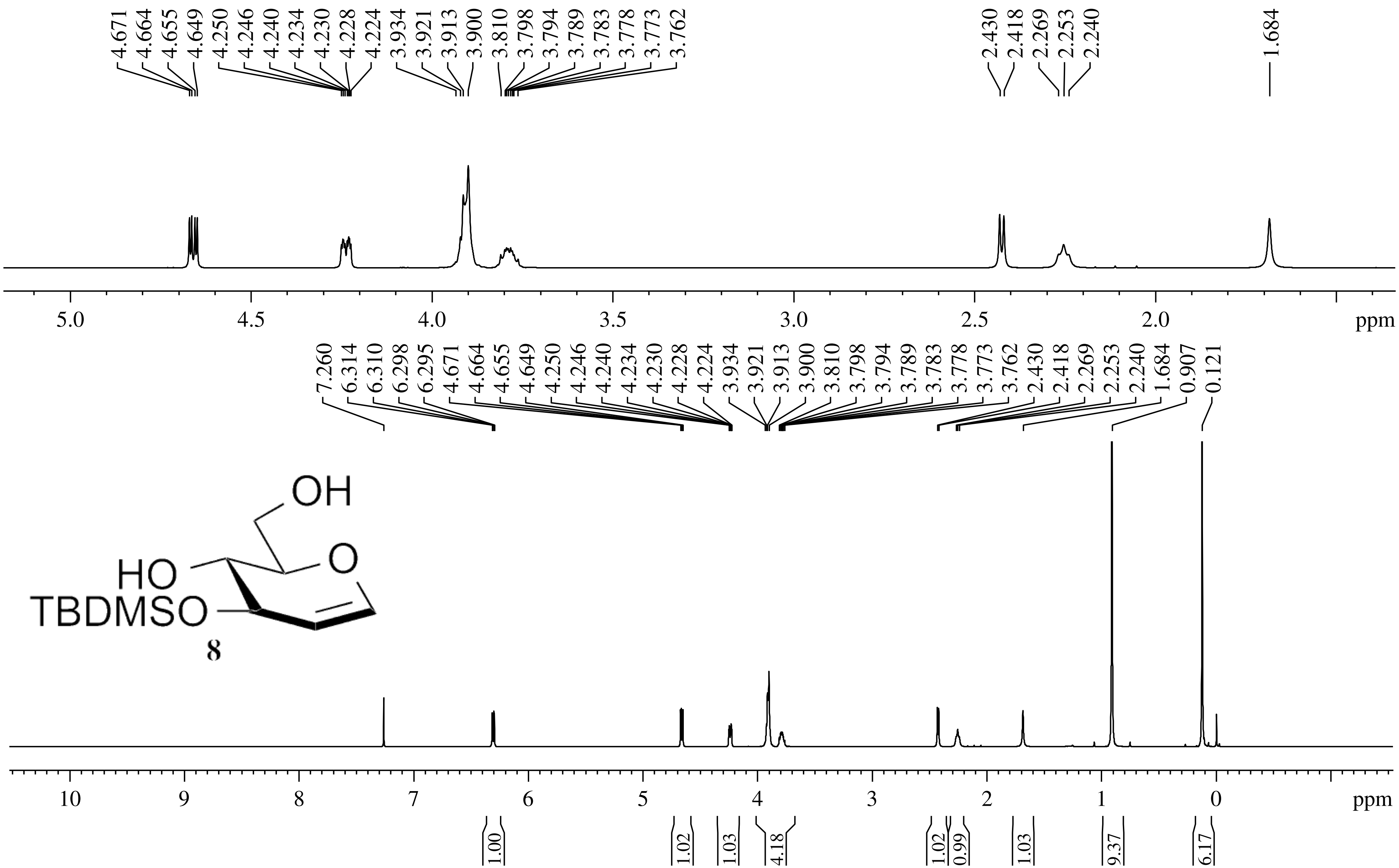


7

^{13}C NMR, $CDCl_3$, 100 MHz

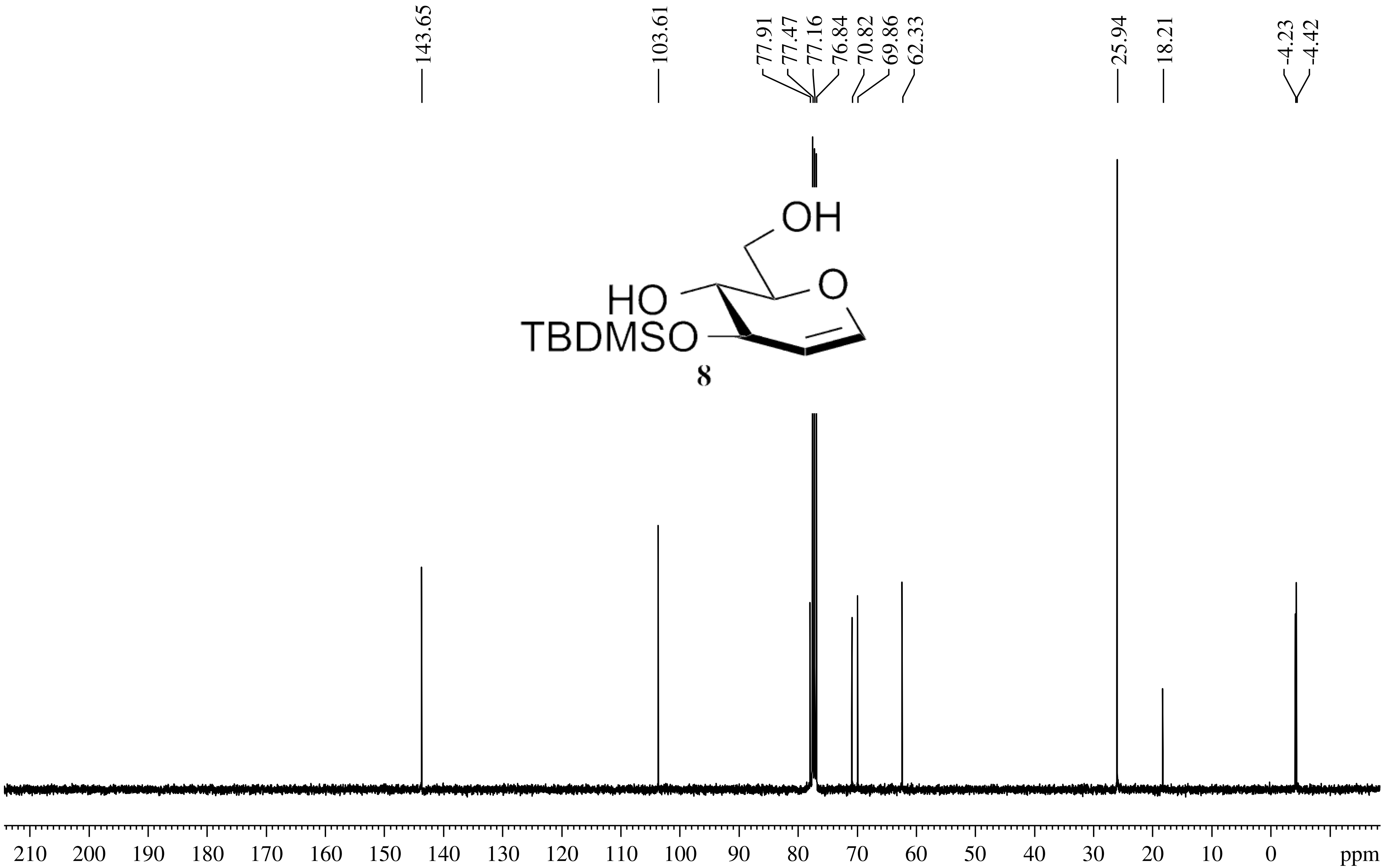


^1H NMR, $CDCl_3$, 400 MHz

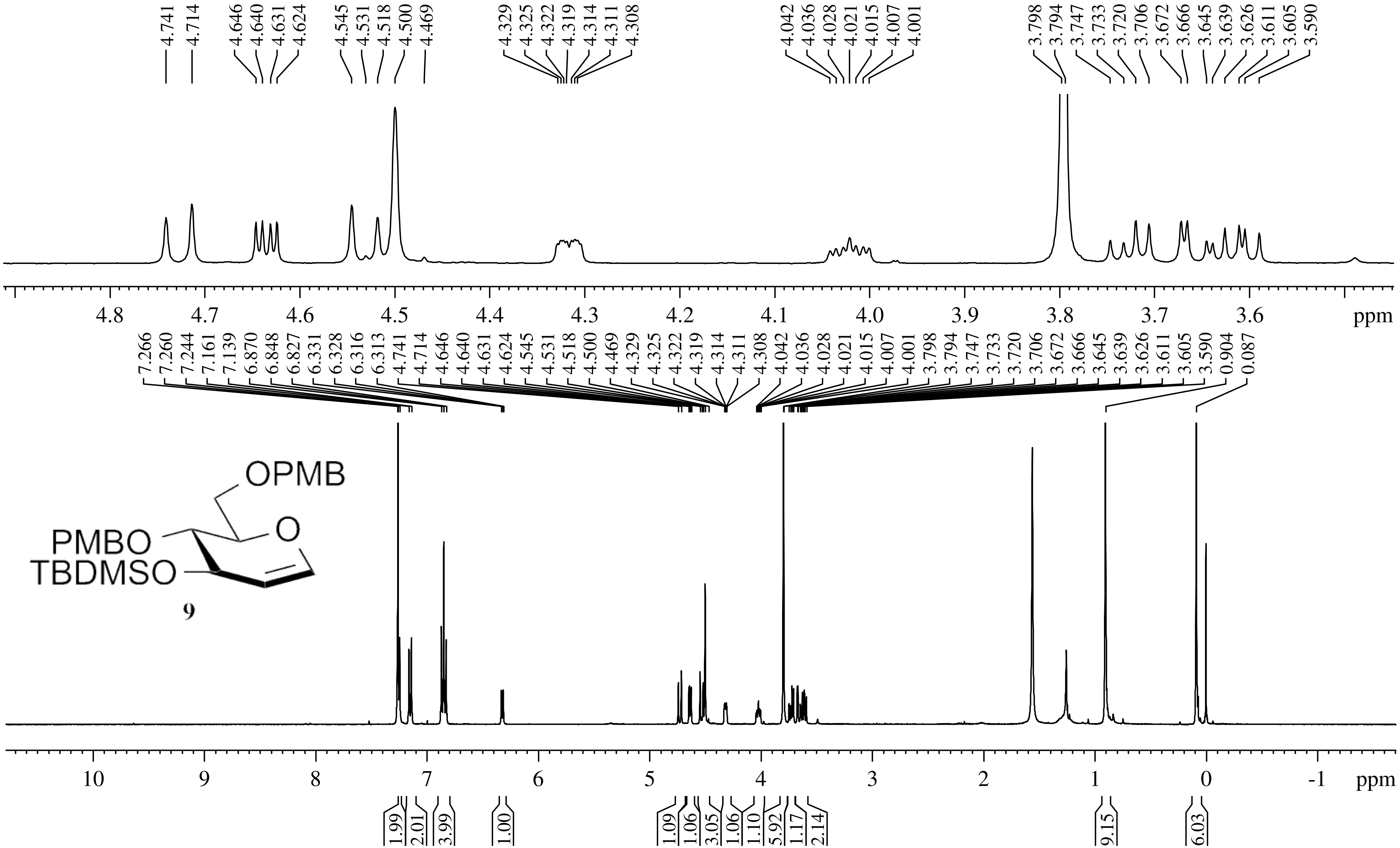


8

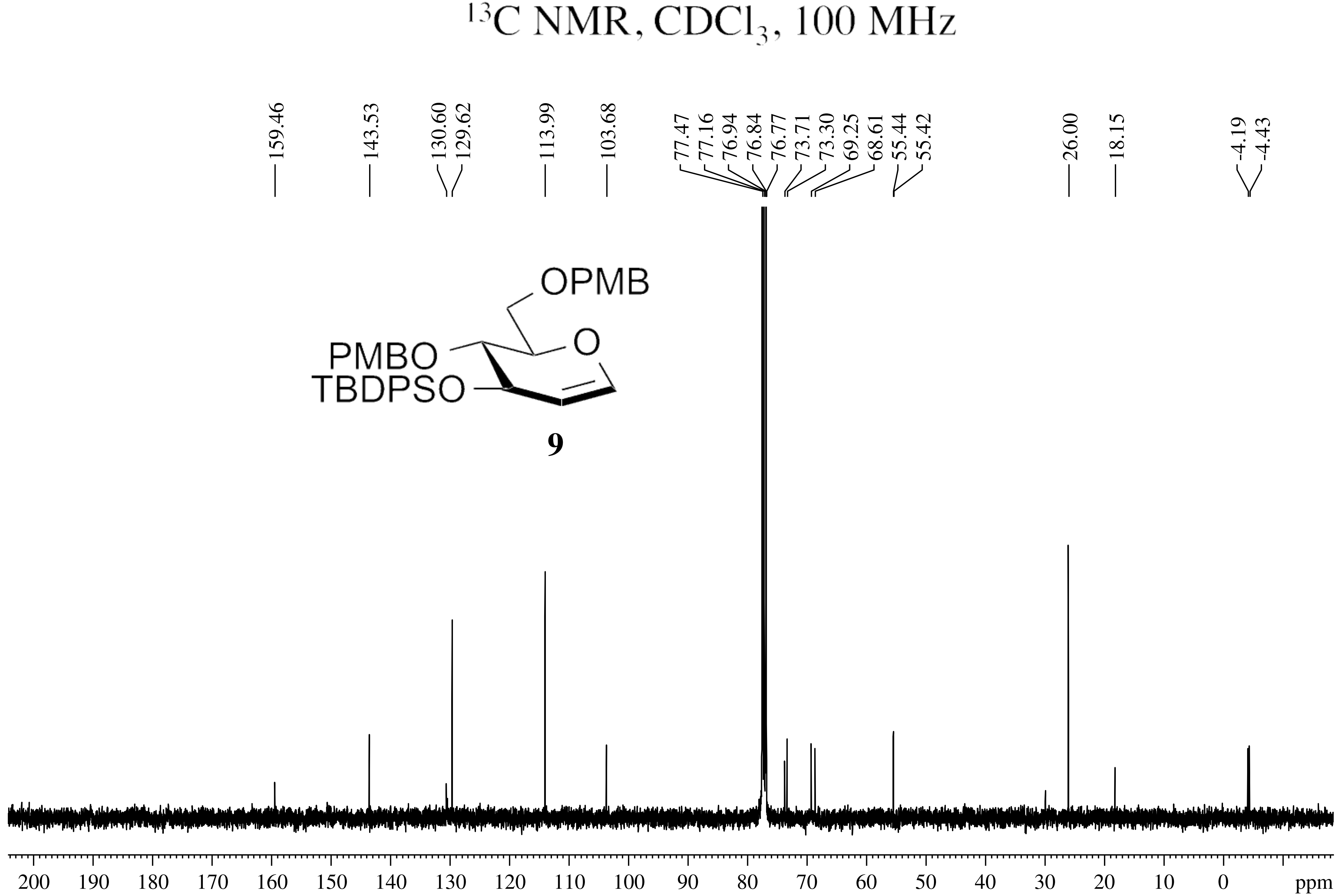
^{13}C NMR, $CDCl_3$, 100 MHz



^{1}H NMR, $CDCl_3$, 400 MHz

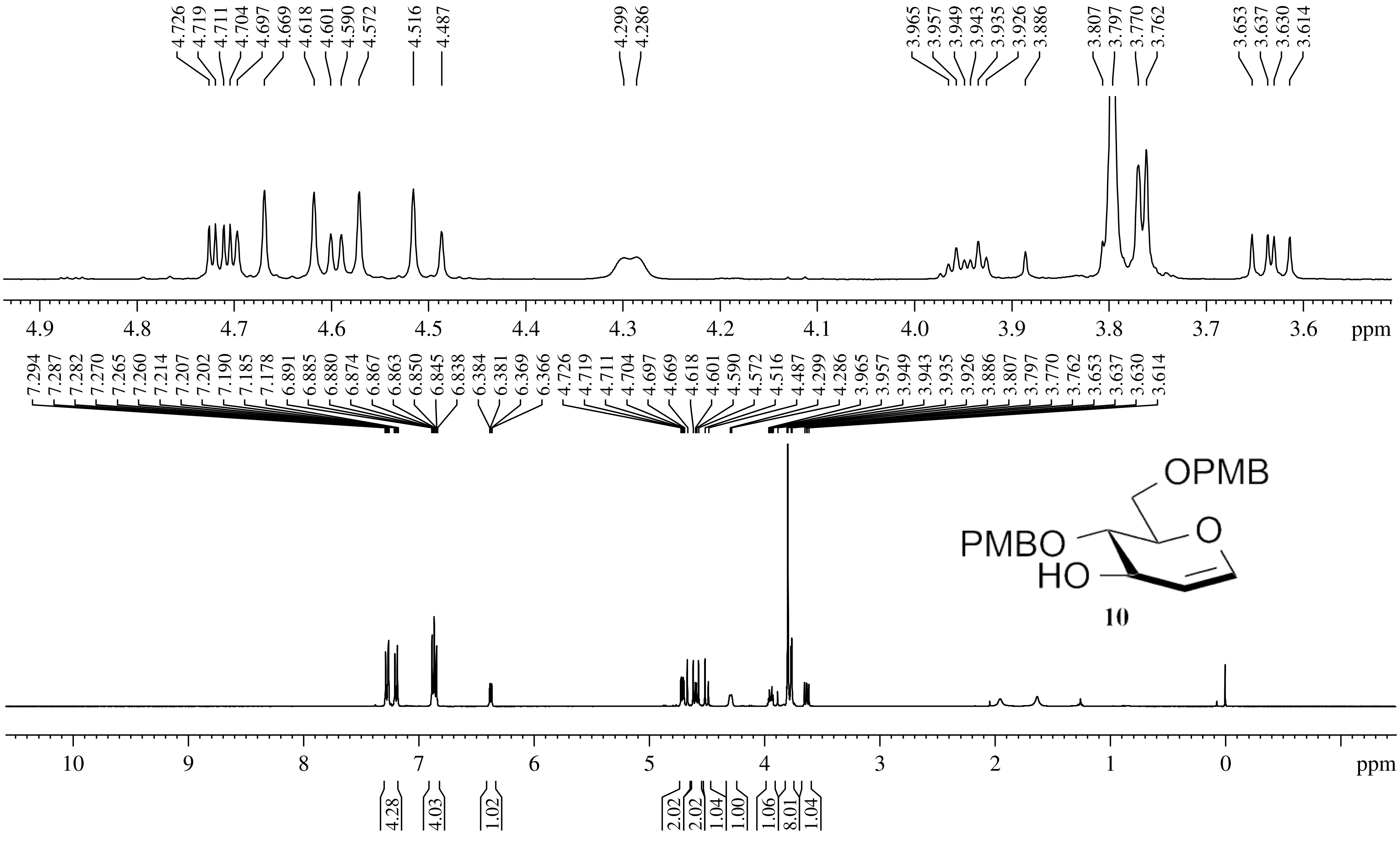


9



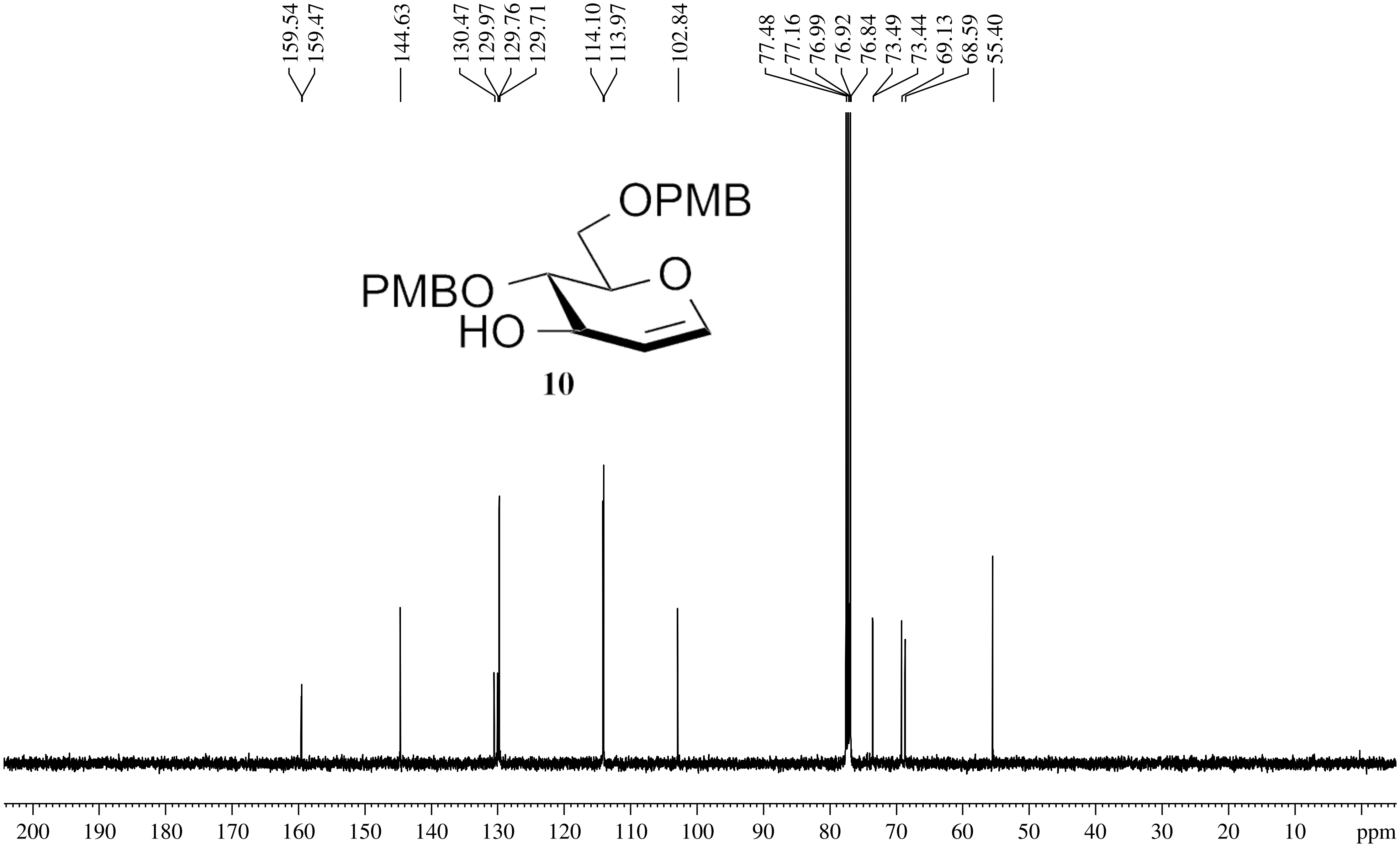
13C NMR, CDCl3, 100 MHz
159.46
143.53
130.60
129.62
113.99
103.68
77.47
77.16
76.94
76.84
76.77
73.71
73.30
69.25
68.61
55.44
55.42
26.00
18.15
-4.19
-4.43
OPMB
O
PMBO
TBDPSO
9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

^{1}H NMR, $CDCl_3$, 400 MHz

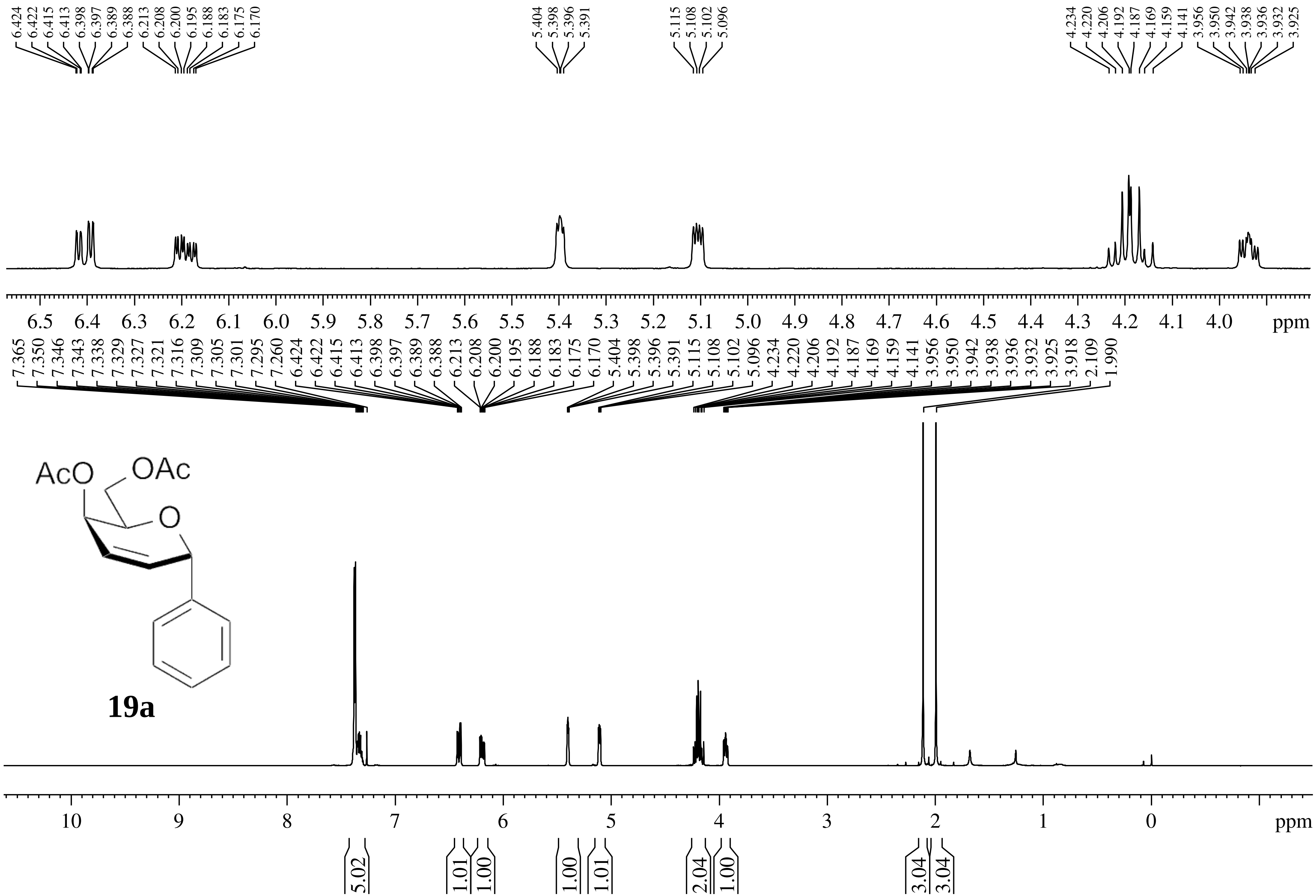


10

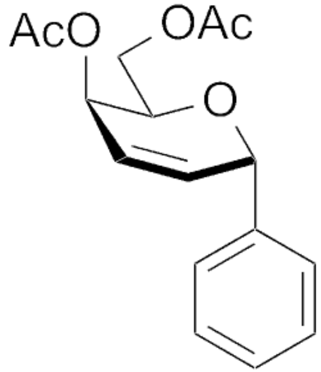
^{13}C NMR, $CDCl_3$, 100 MHz



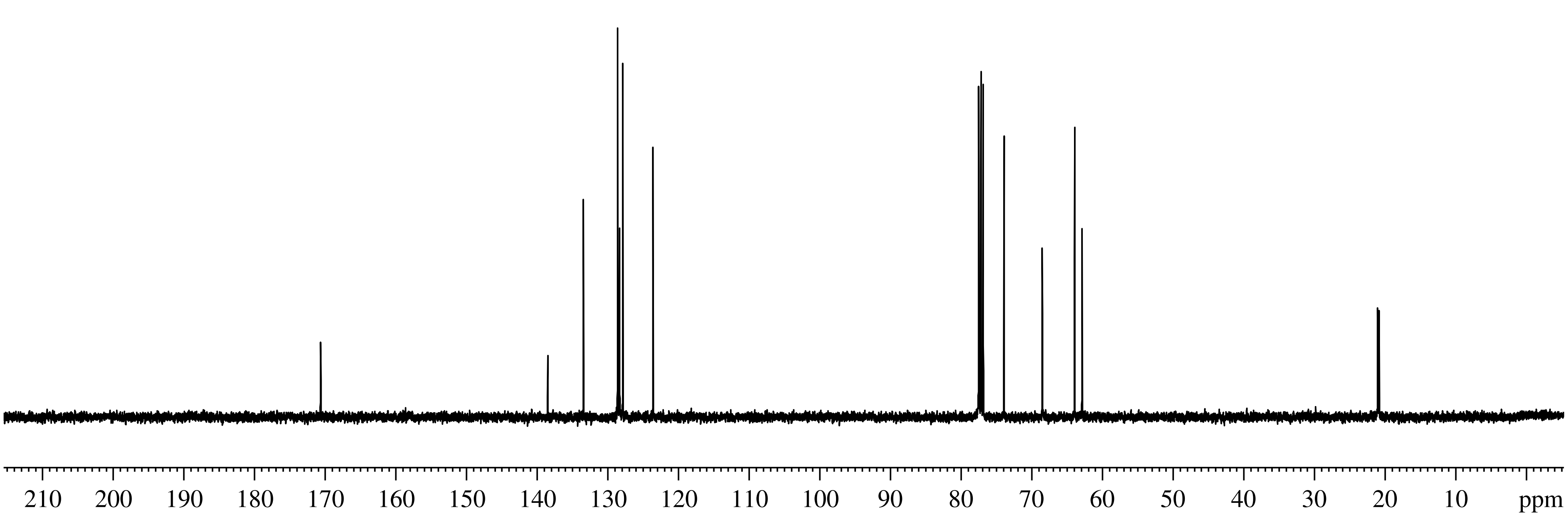
1H NMR, CDCl3, 400 MHz



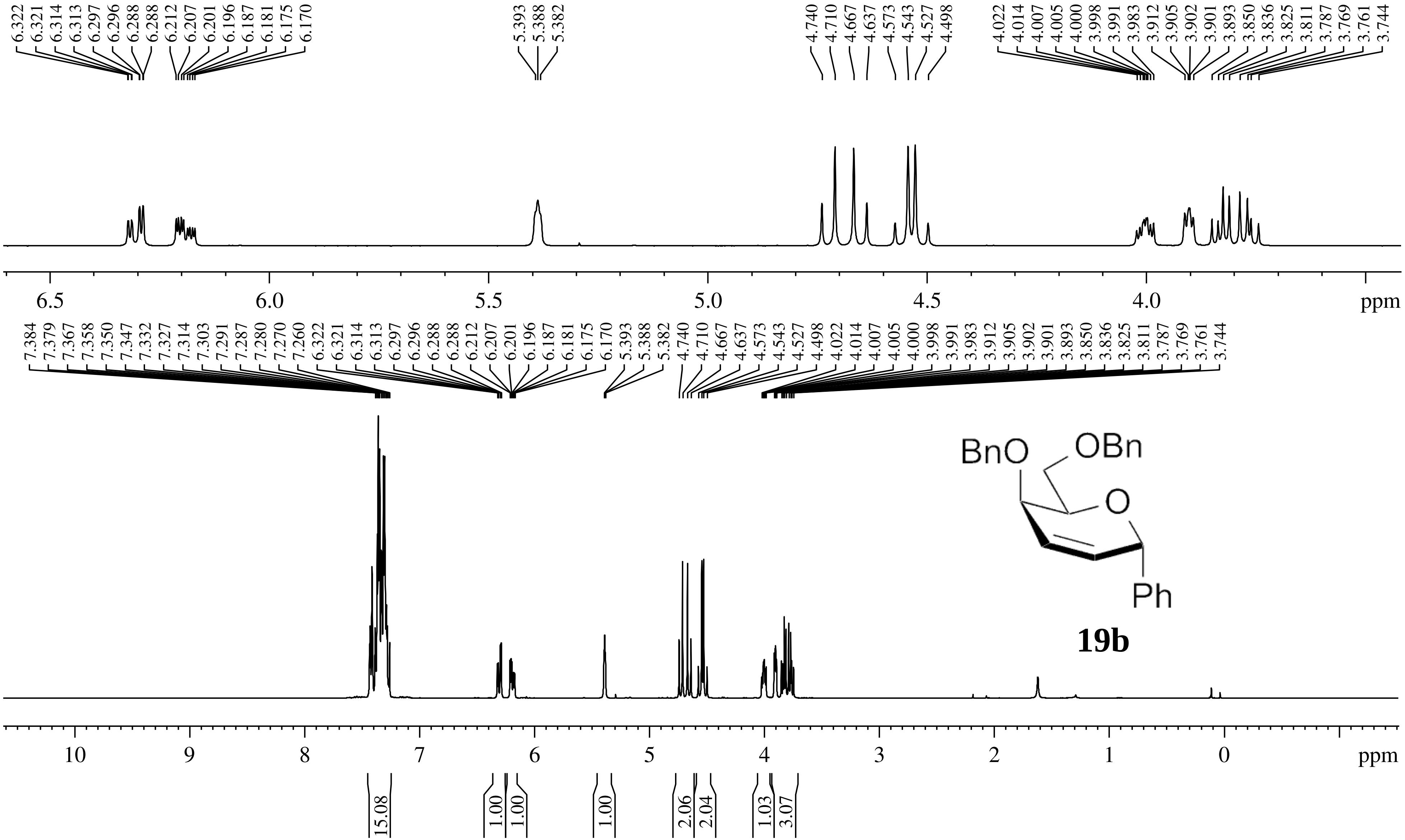
13C NMR, CDCl3, 100 MHz



19a

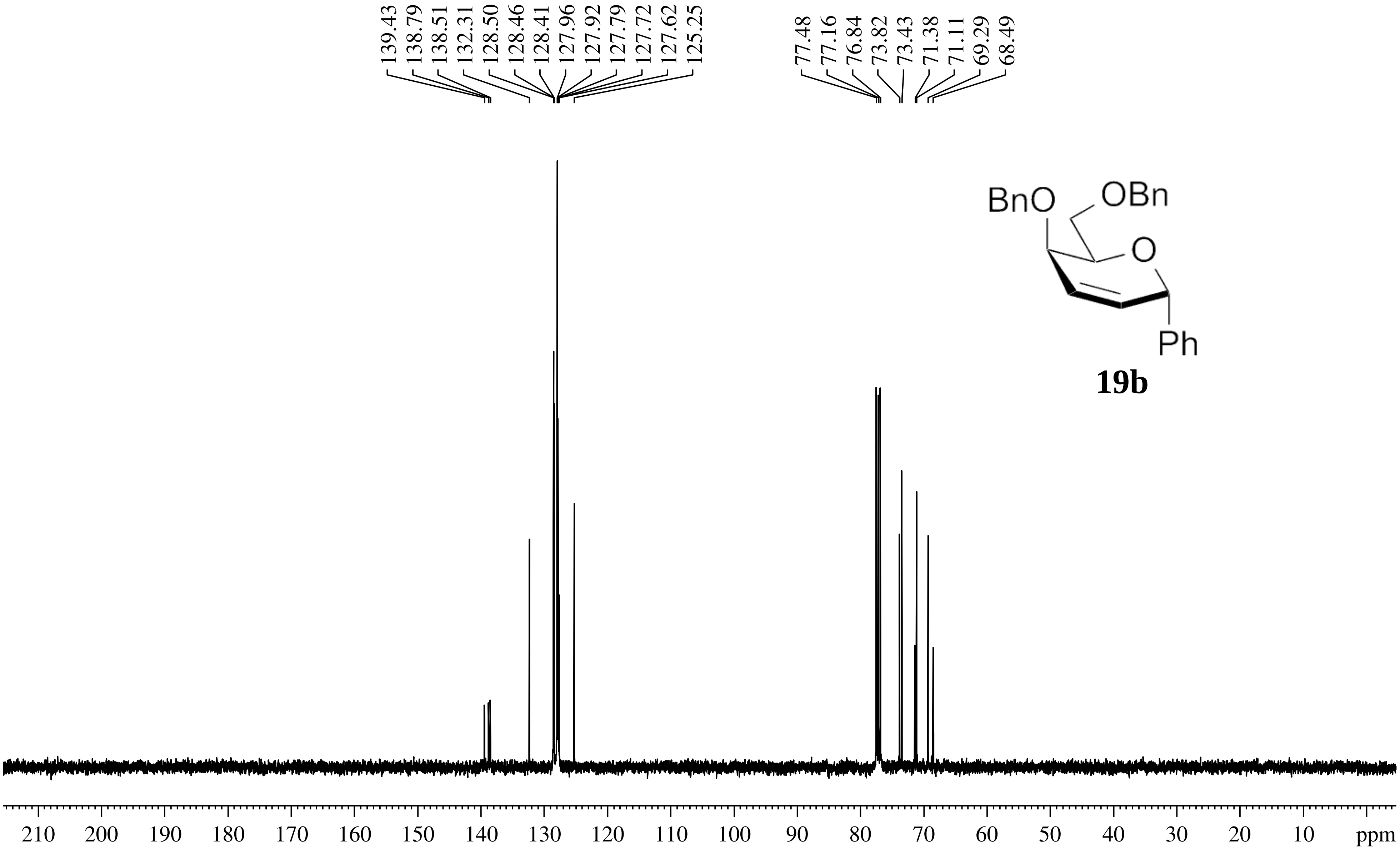


^{1}H NMR, $CDCl_3$, 400 MHz



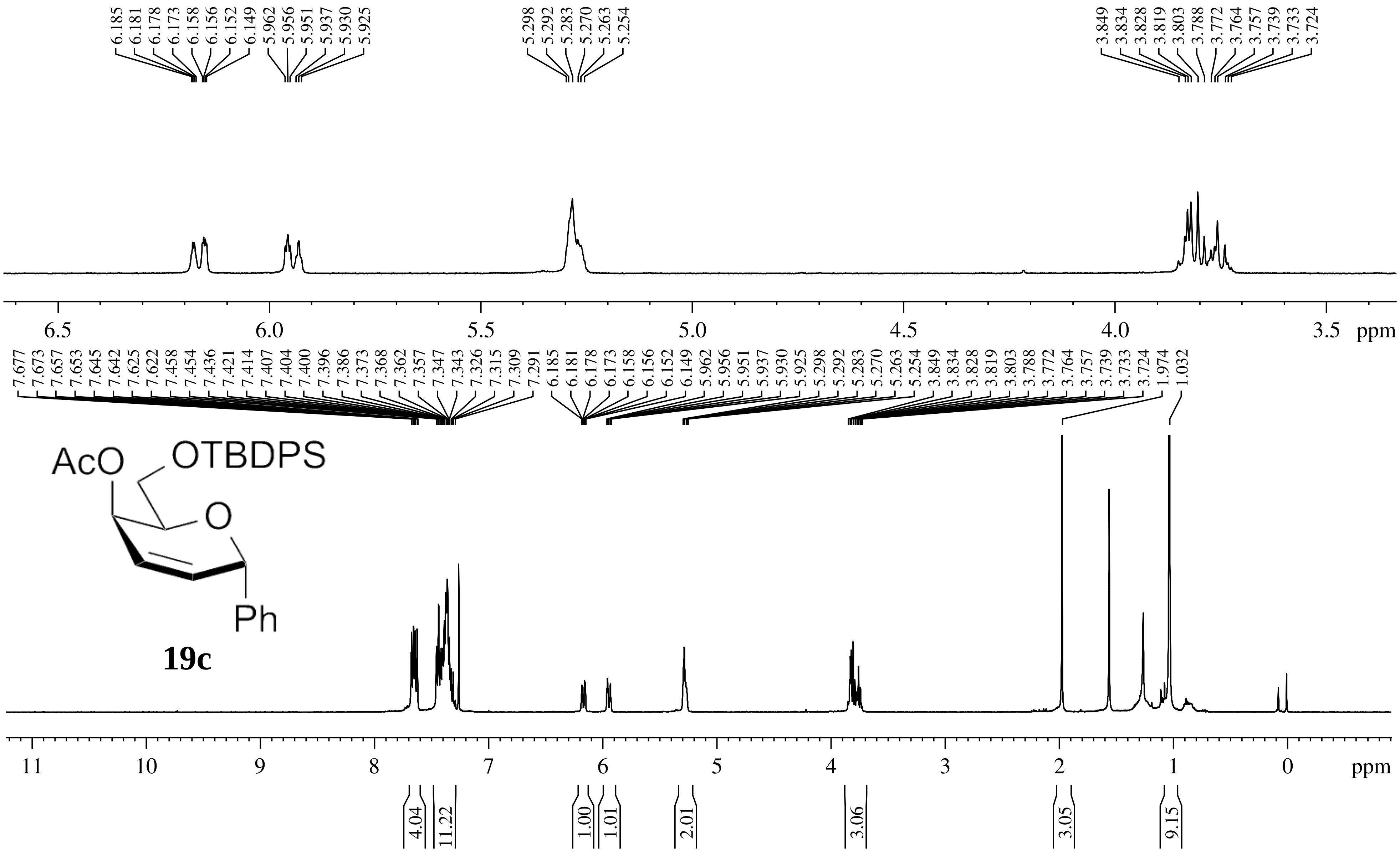
19b

^{13}C NMR, $CDCl_3$, 100 MHz

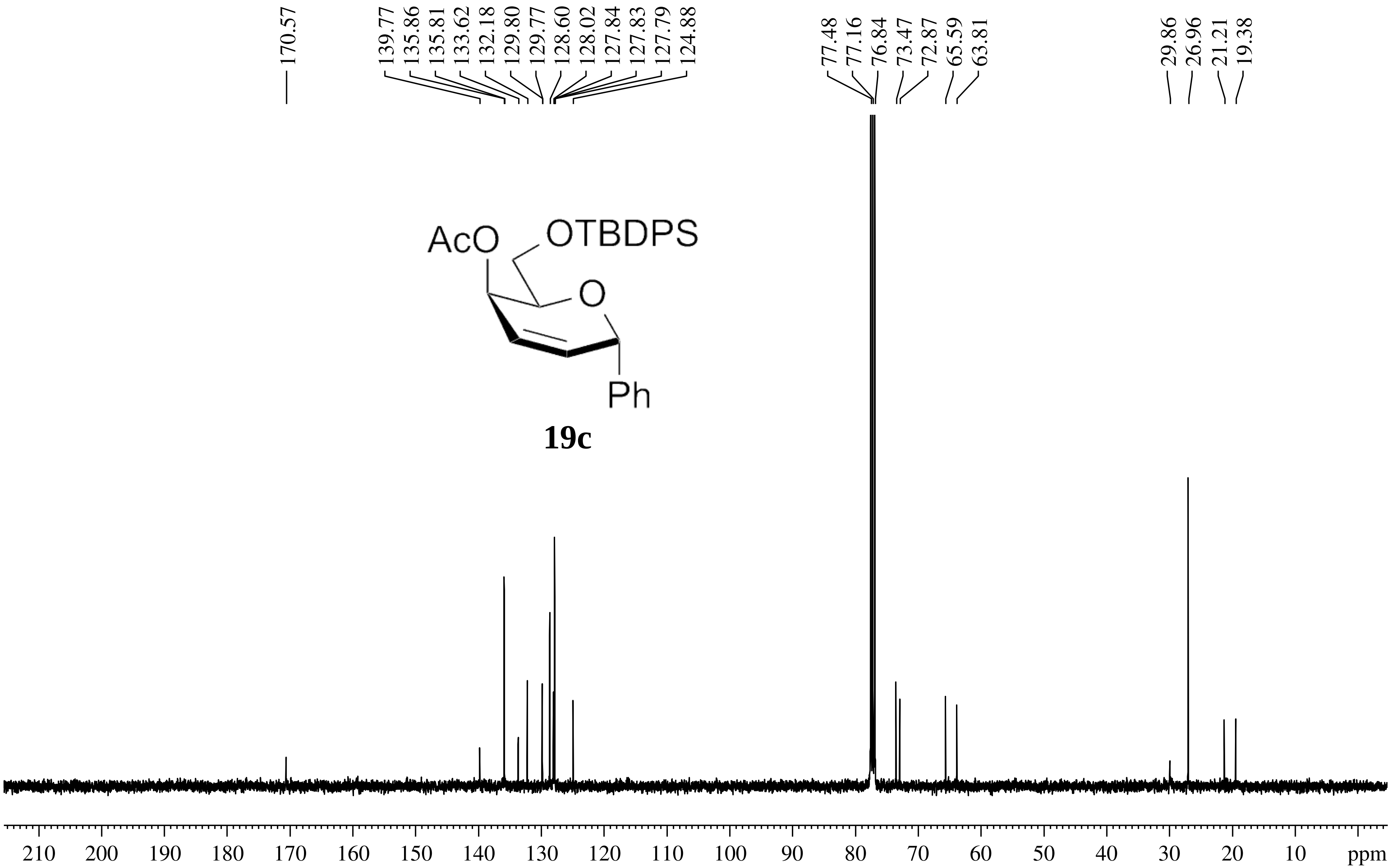


19b

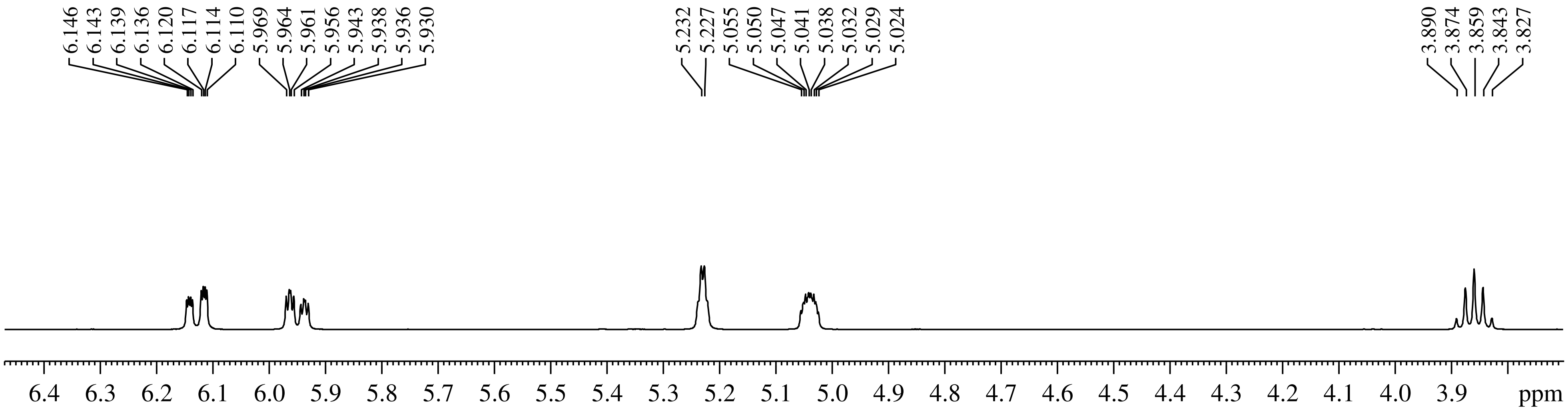
^{1}H NMR, $CDCl_3$, 400 MHz

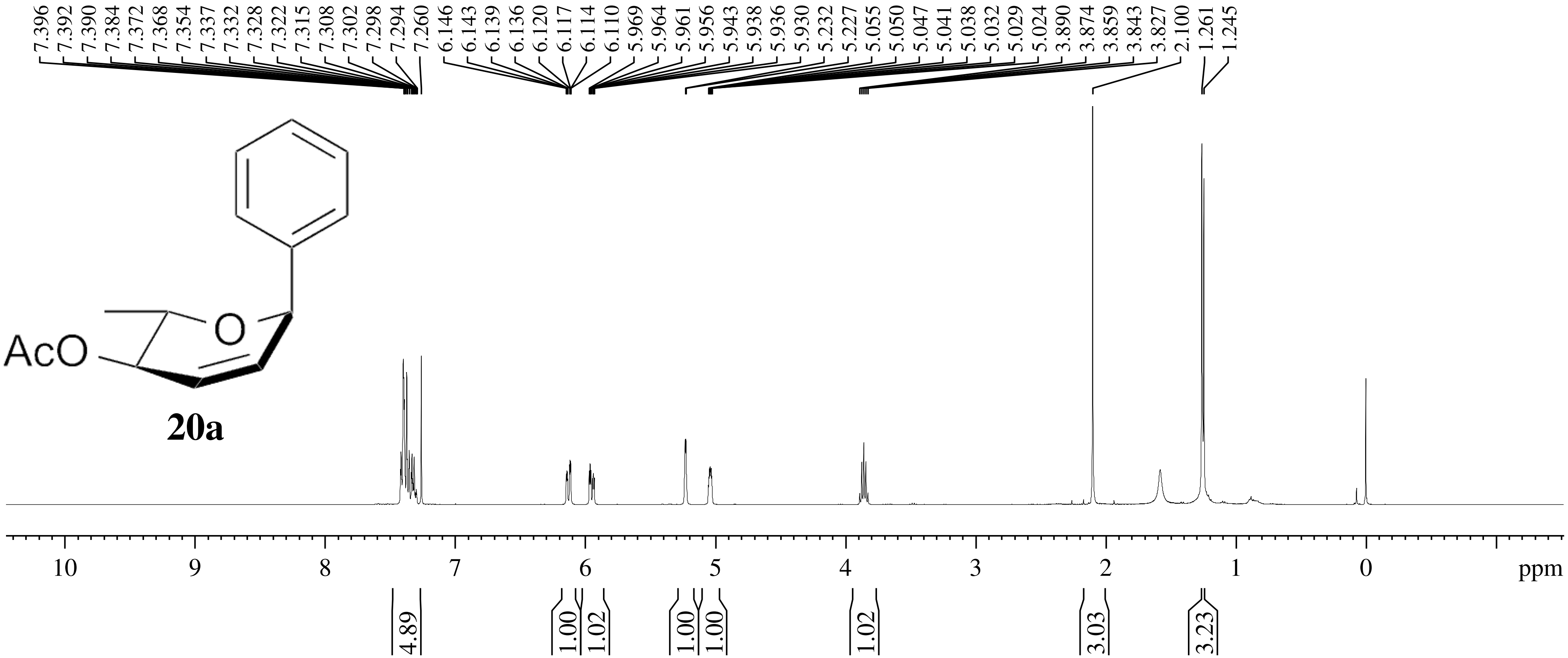


^{13}C NMR, $CDCl_3$, 100 MHz

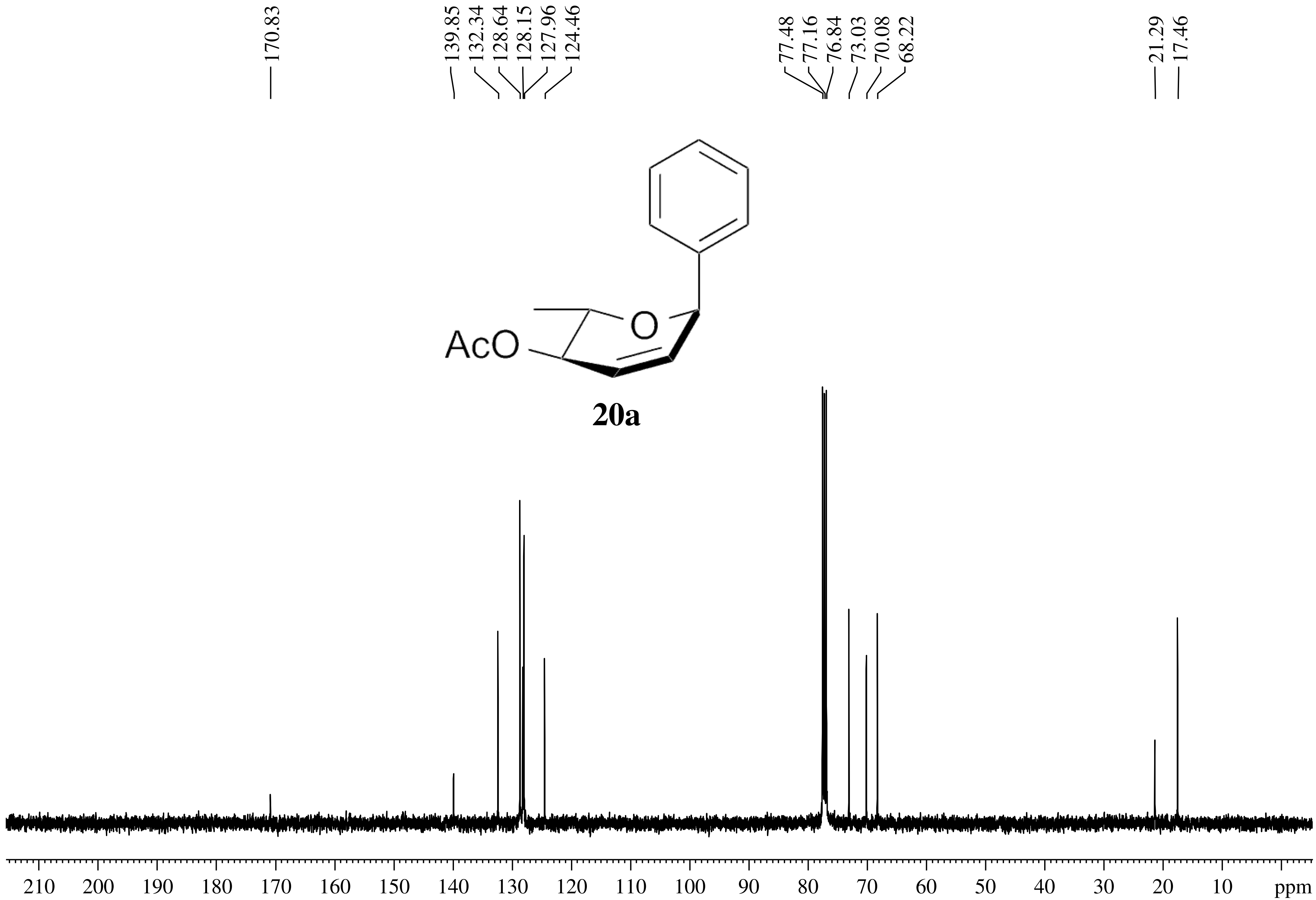


1H NMR, CDCl3, 400 MHz

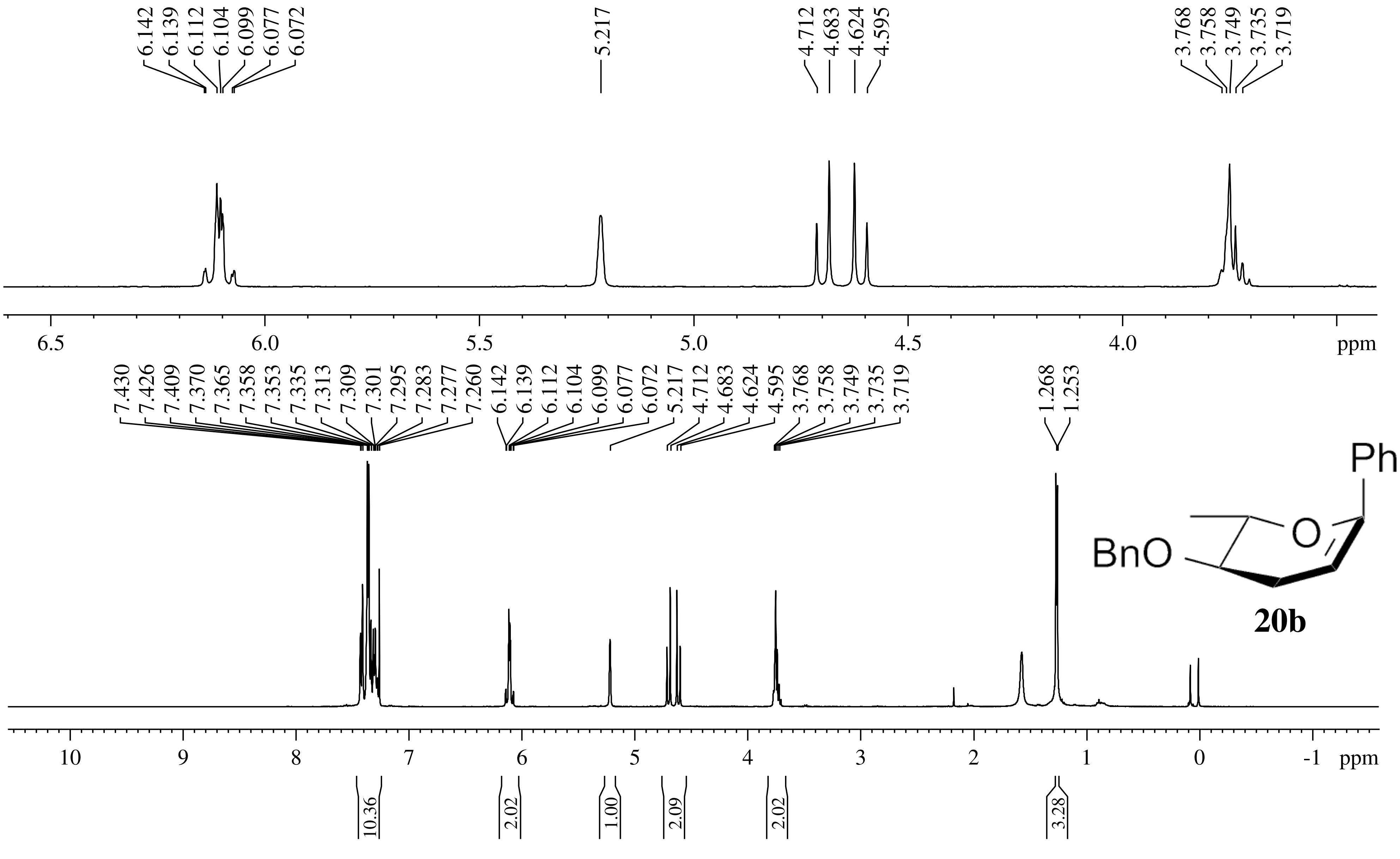




13C NMR, CDCl3, 100 MHz



^1H NMR, $CDCl_3$, 400 MHz



20b

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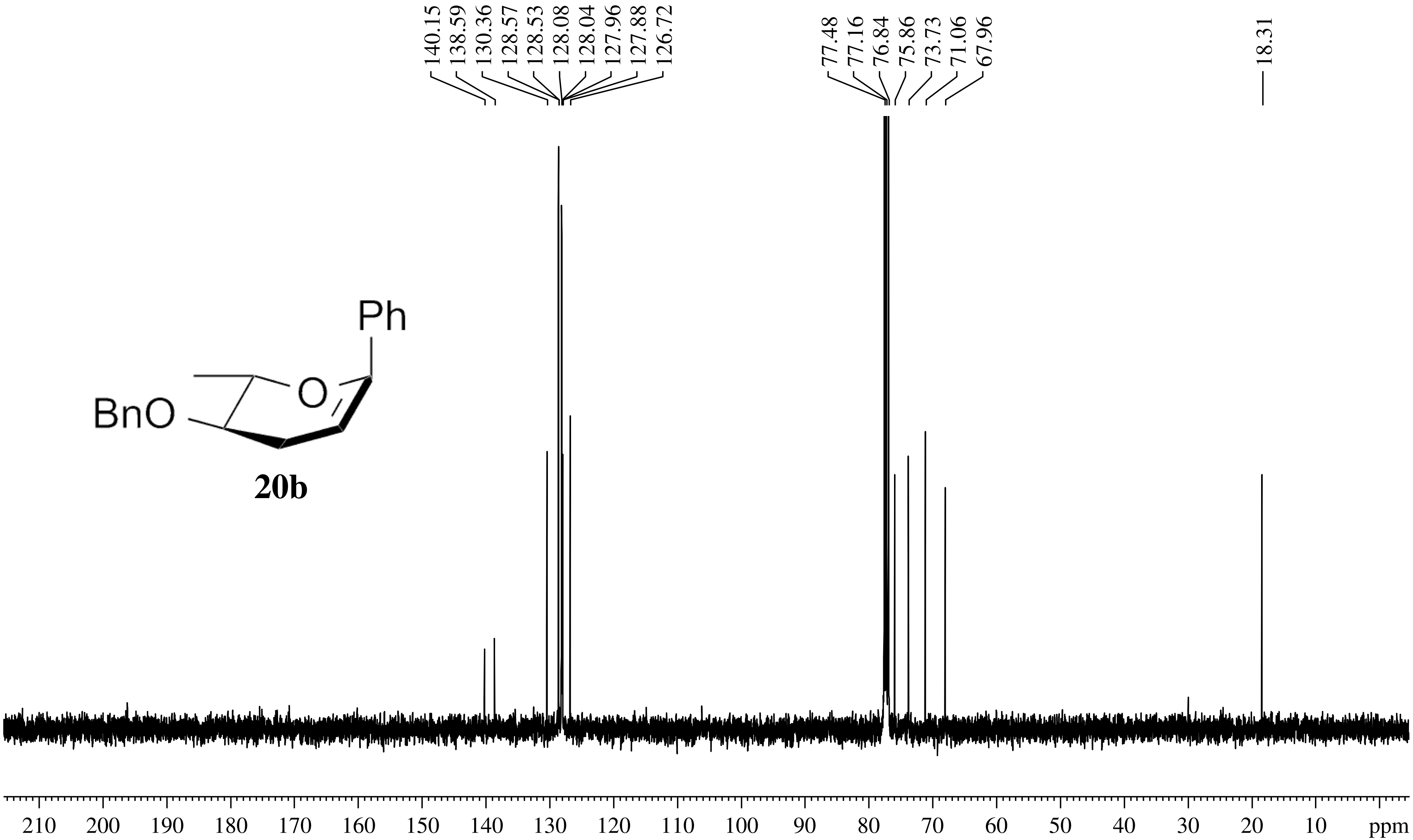
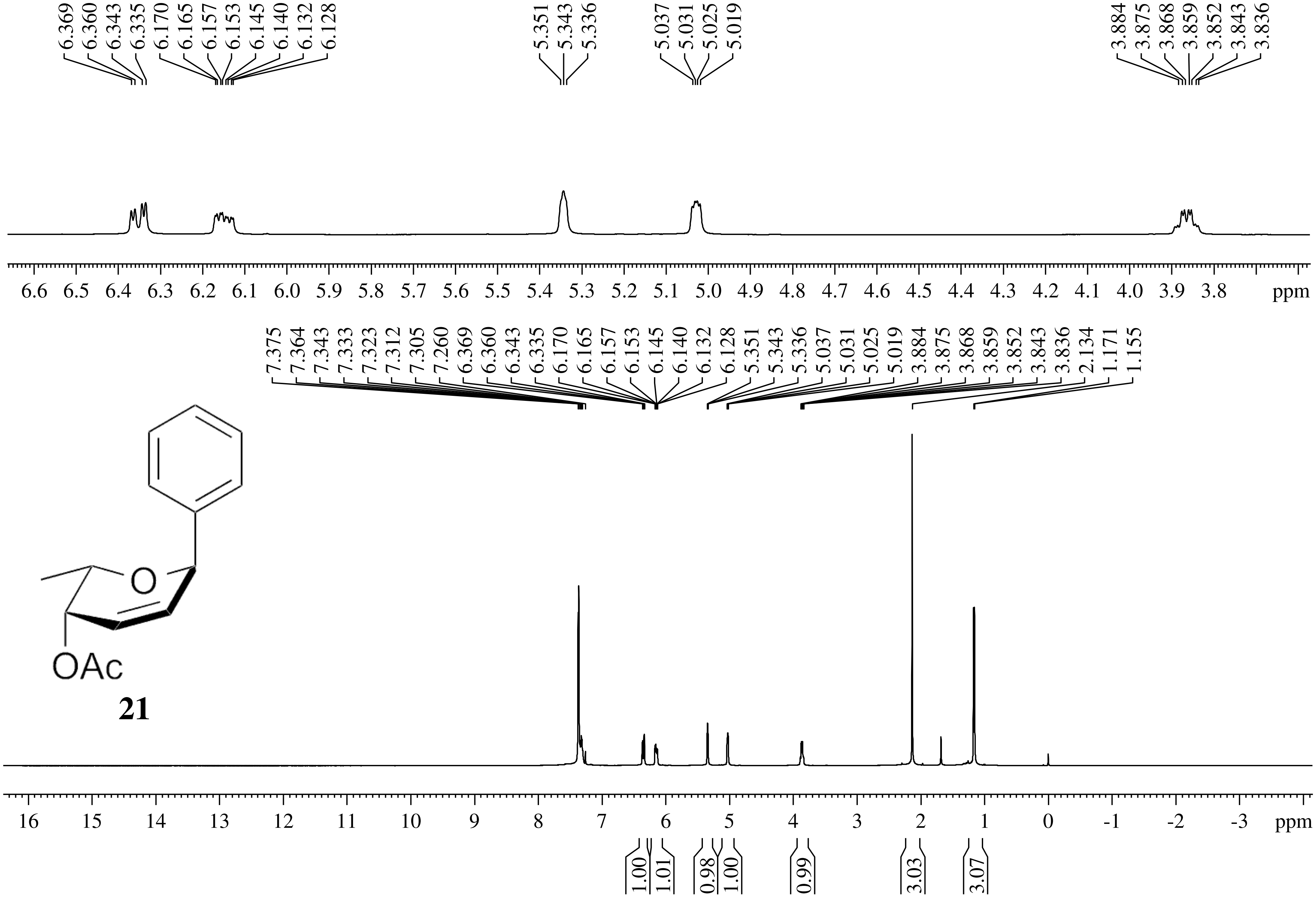
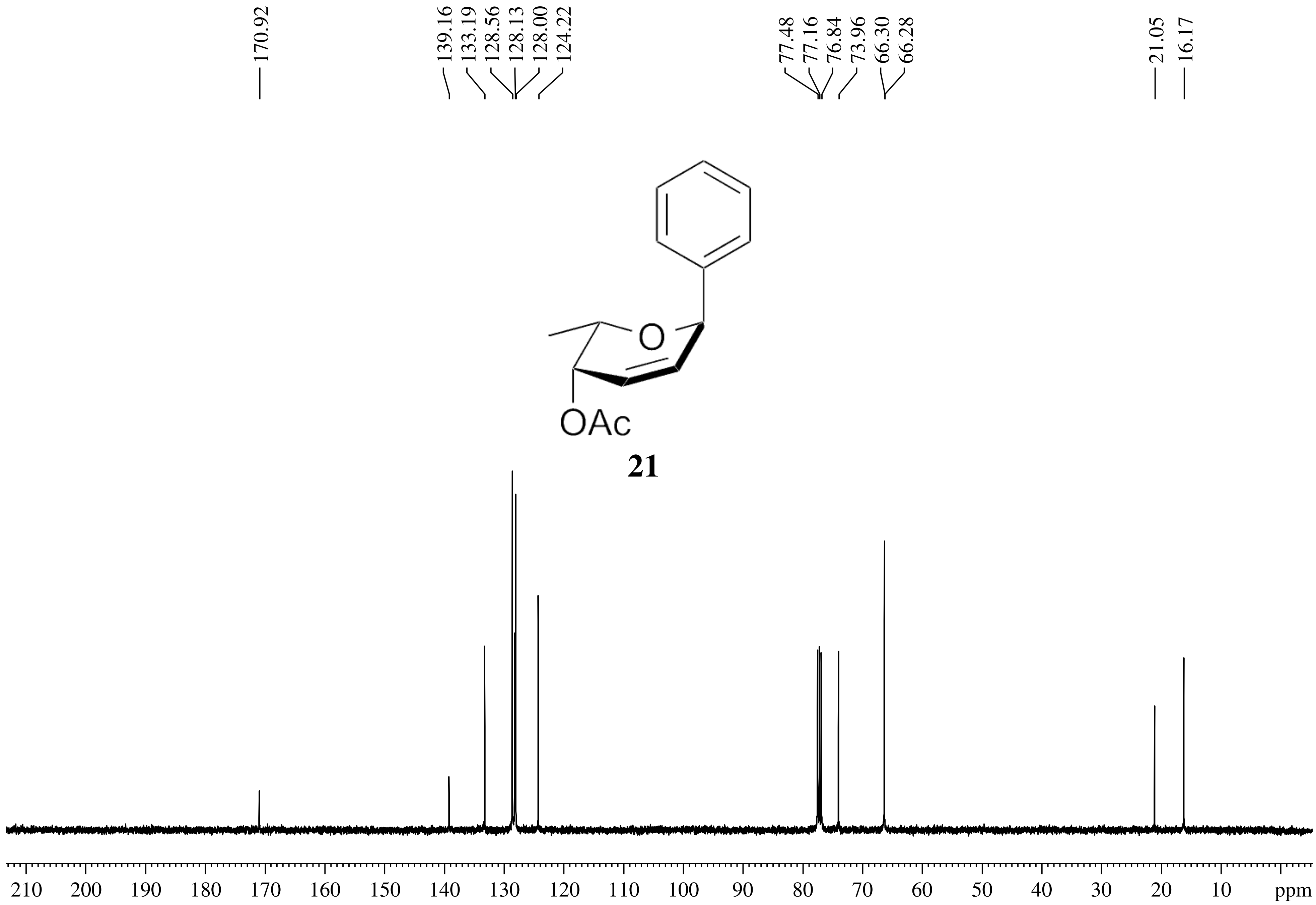


1H NMR, CDCl3, 400 MHz

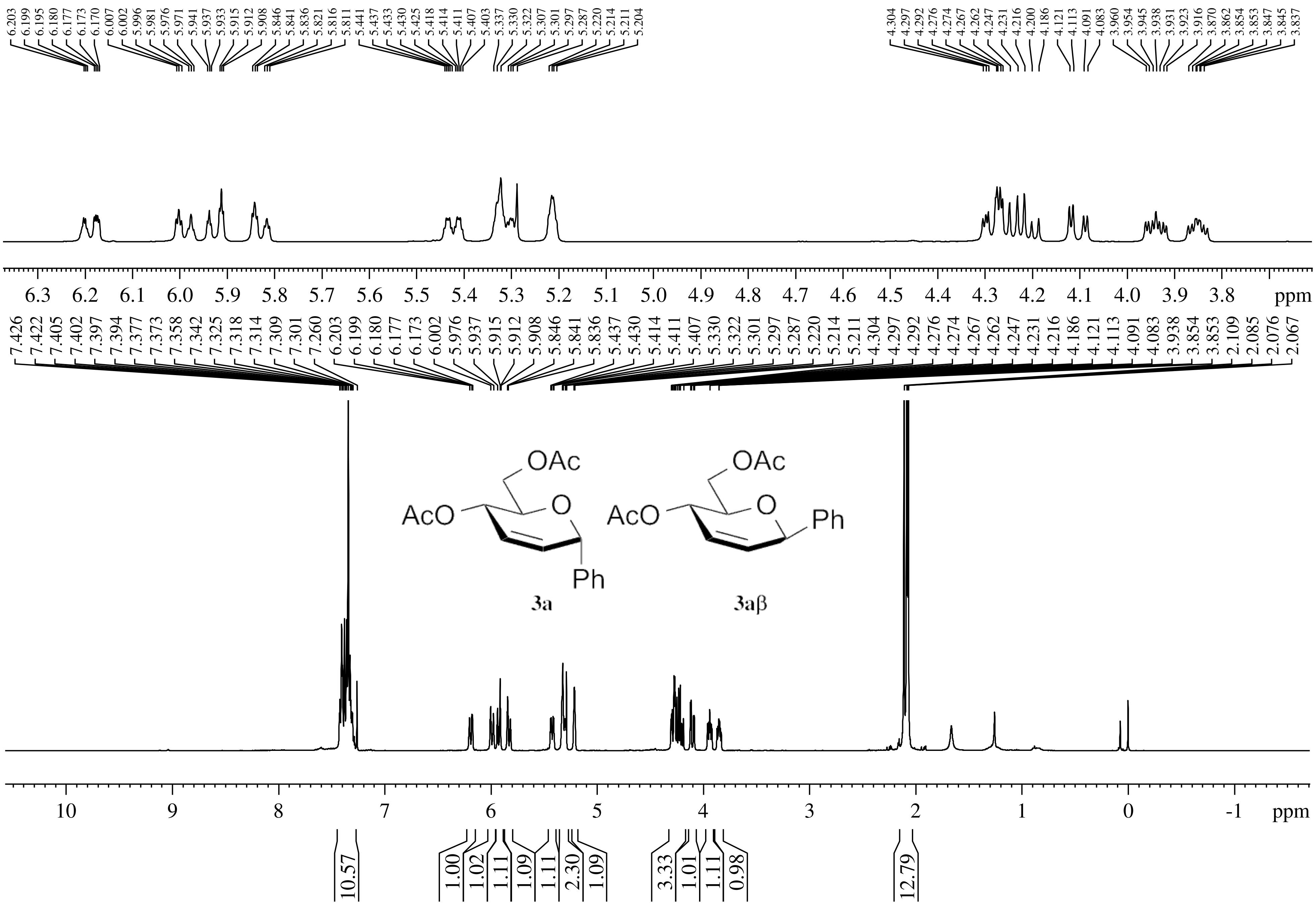


21

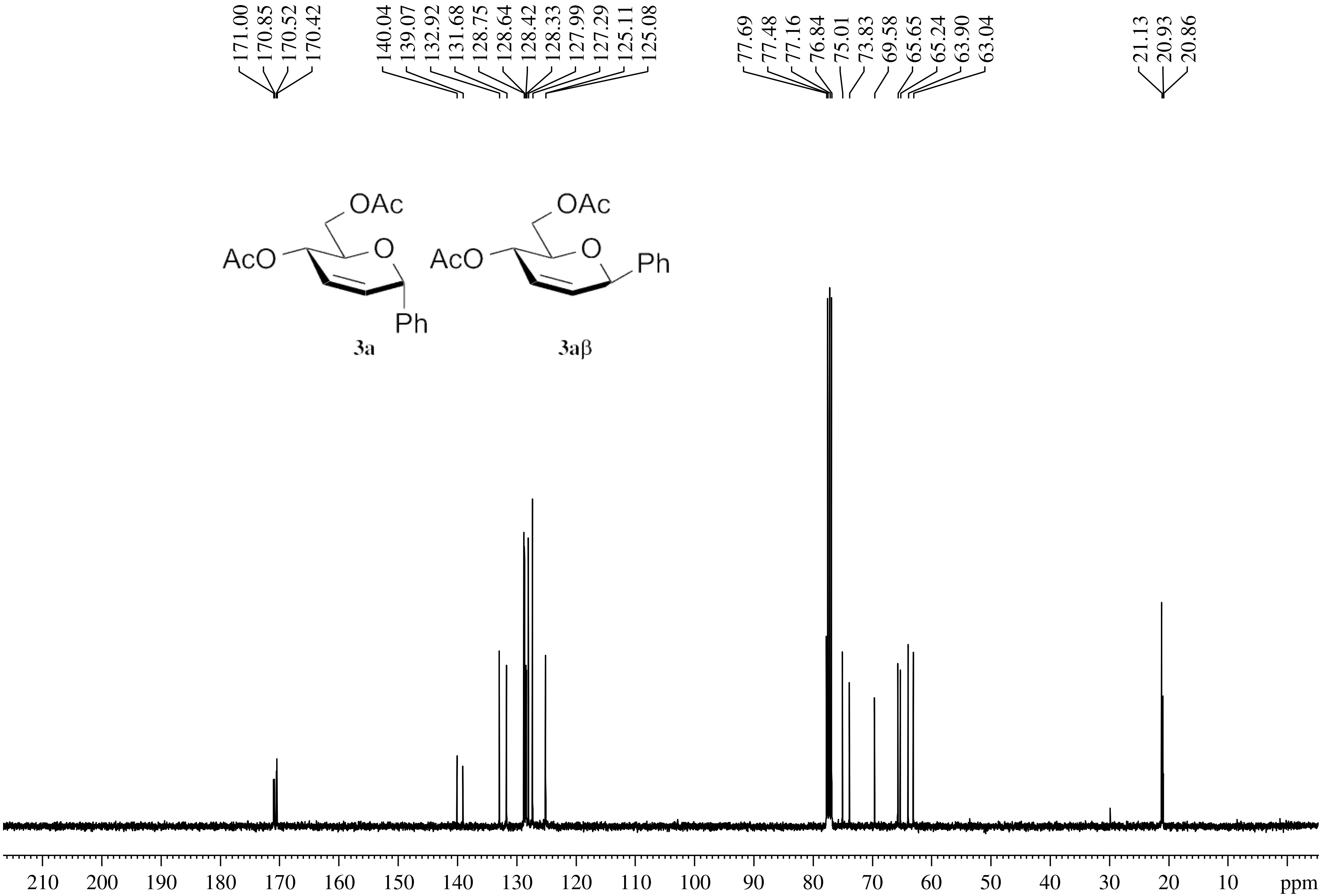
13C NMR, CDCl3, 100 MHz



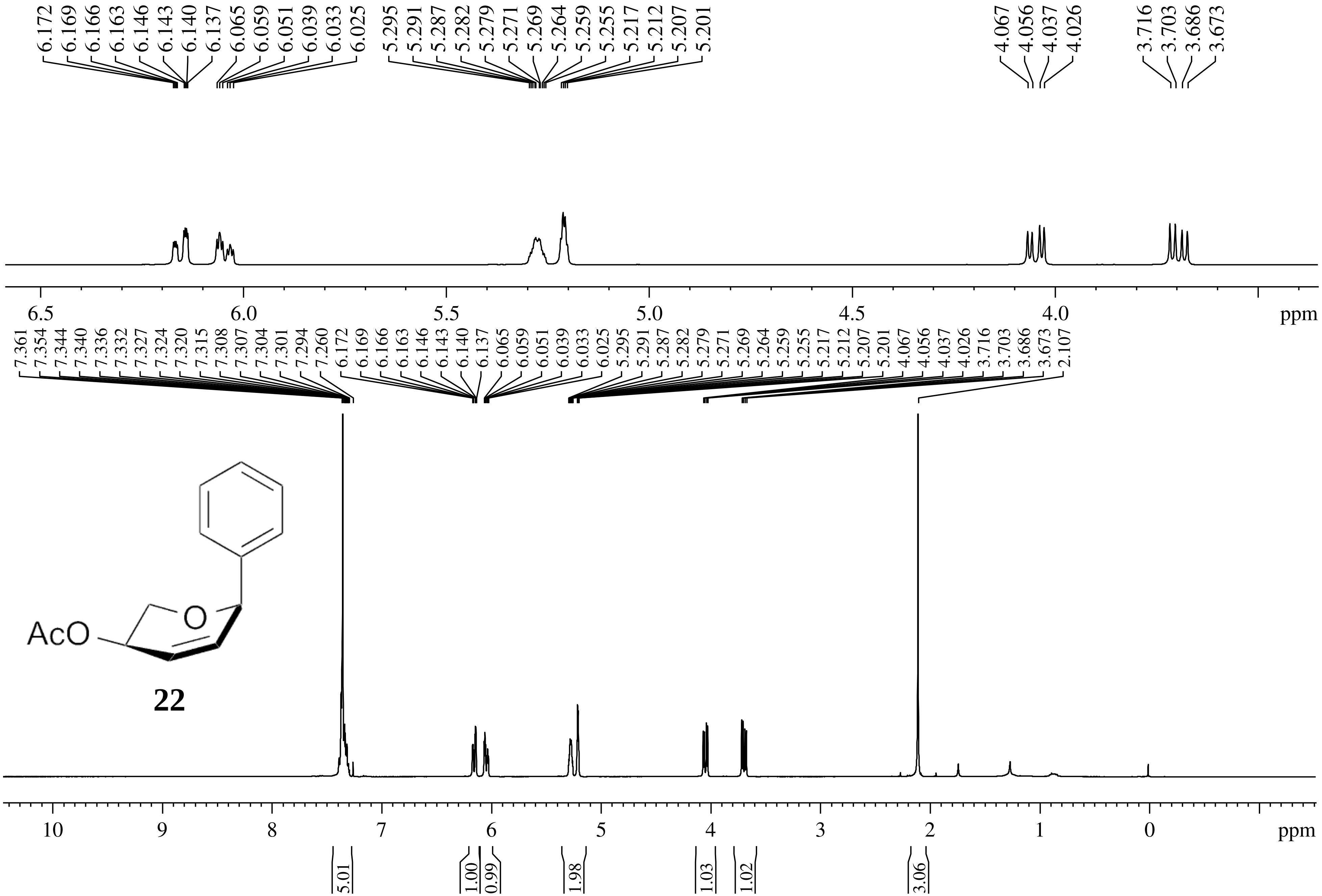
1H NMR, CDCl3, 400 MHz



13C NMR, CDCl3, 100 MHz

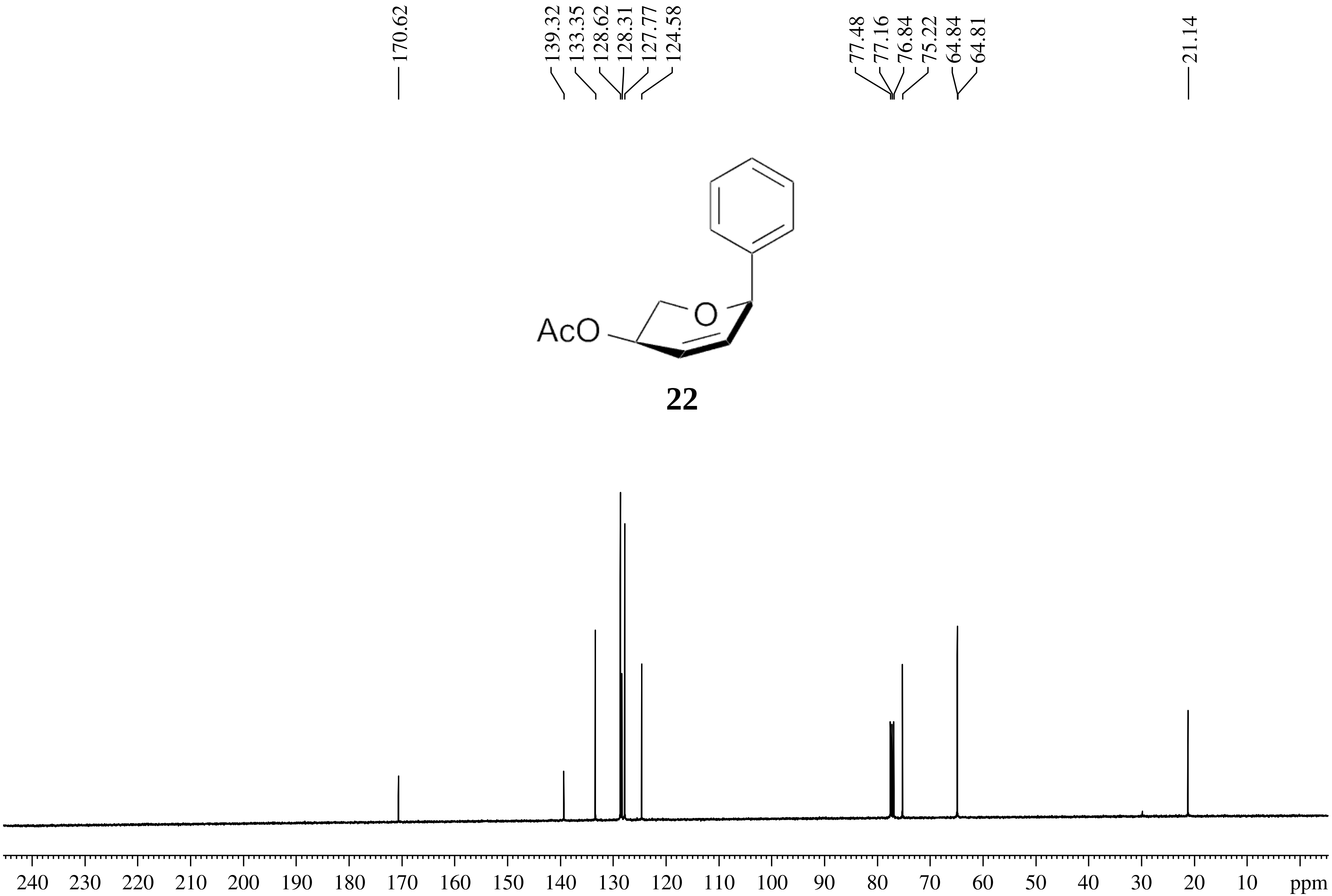


1H NMR, CDCl3, 400 MHz

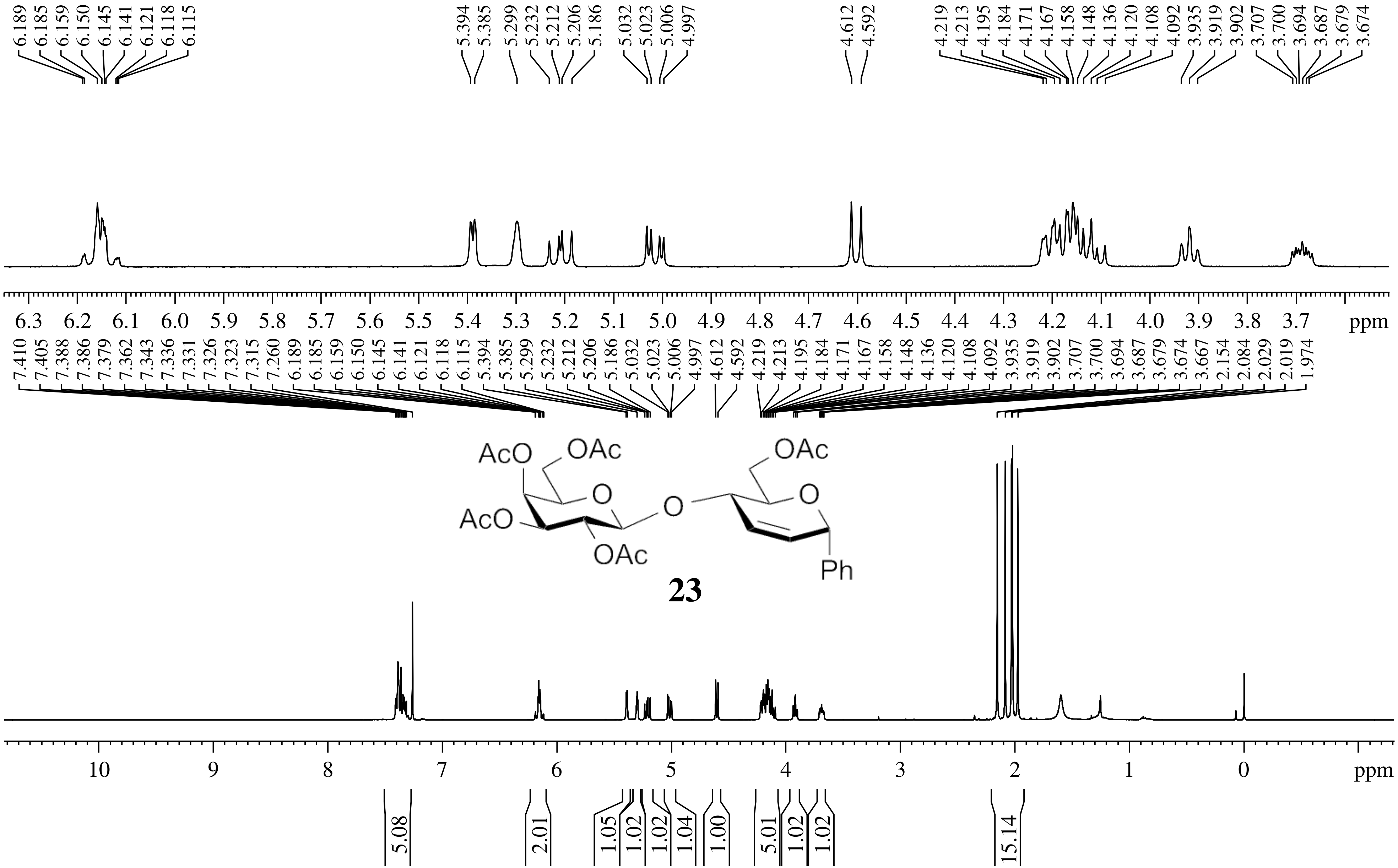


22

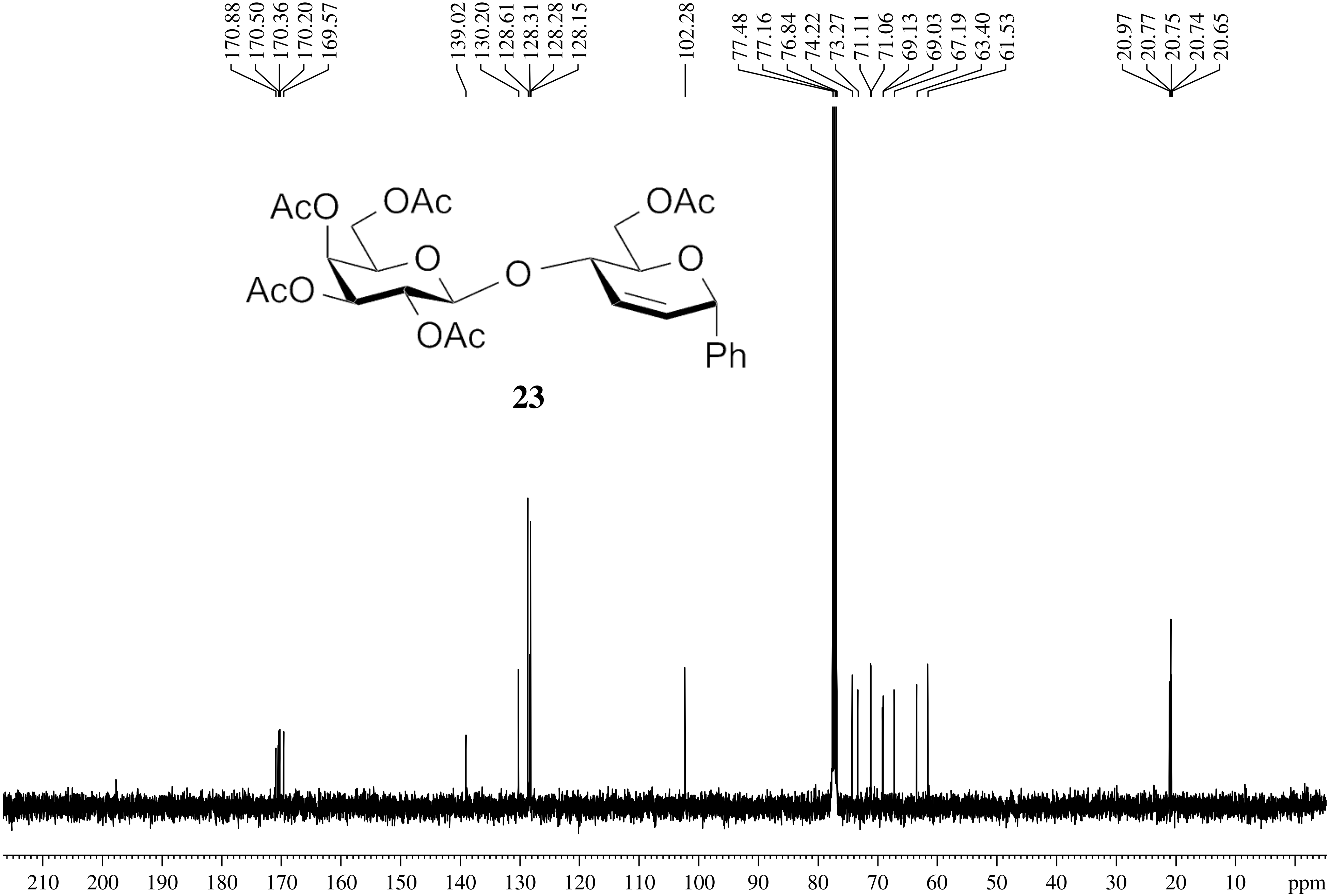
13C NMR, CDCl3, 100 MHz



^{1}H NMR, $CDCl_3$, 400 MHz

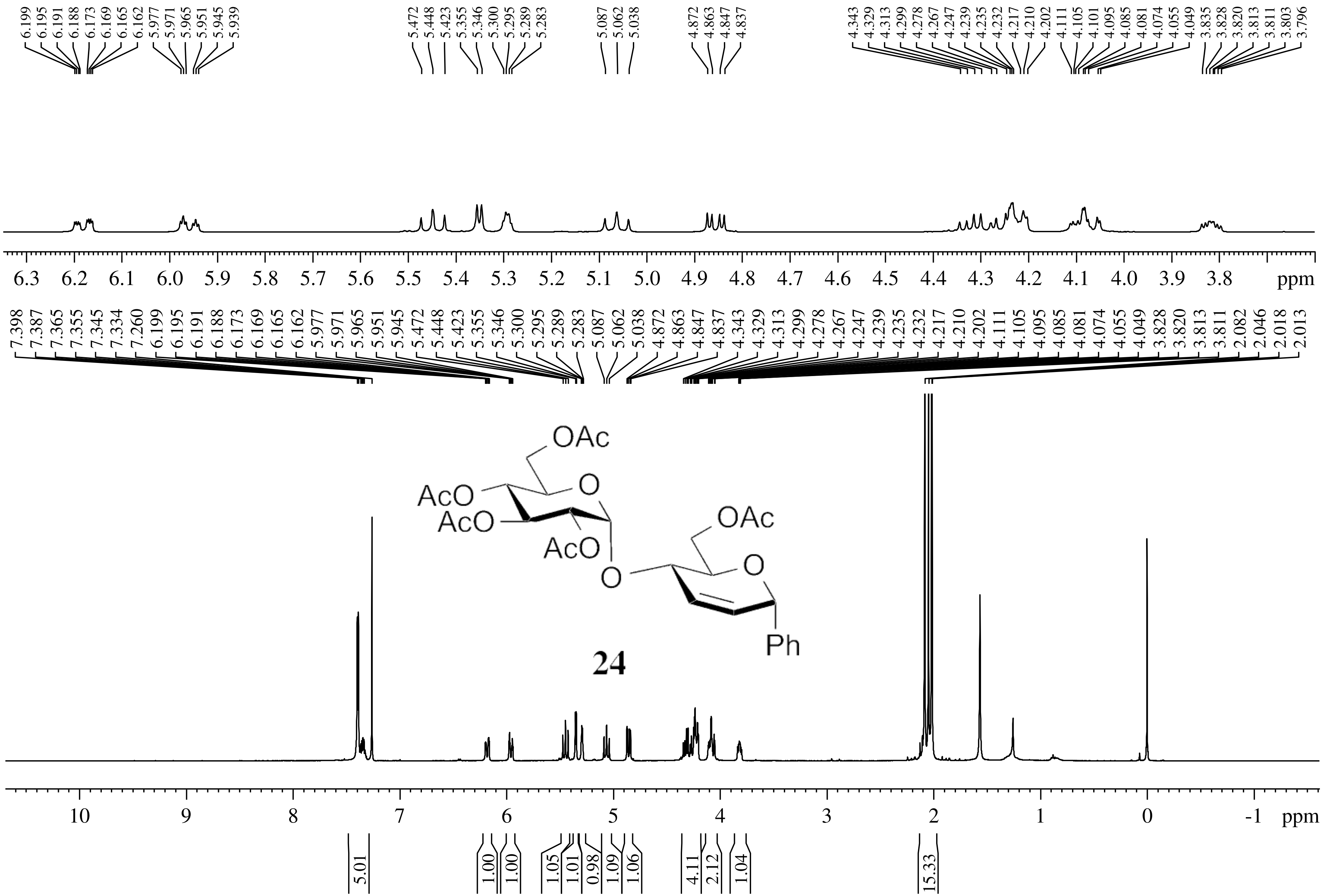


^{13}C NMR, $CDCl_3$, 100 MHz



23

^1H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 100 MHz